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**(54) Filament nonwoven fabrics and method of fabricating the same**

(57) A filament nonwoven fabric and method of fabricating the same. The method comprises the steps of melting a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, said polymer having a melting point of 100°C or more, or a blend of such polymers having a melting point of 100°C or more, said polymer or polymer blend having a melt flow rate of from 10 to 100 g/10 minutes as measured at 190°C. according to ASTM-D-1238 (E), in a temperature range of from (Tm + 20)°C to (Tm + 80)°C, where Tm°C is the melting point of the polymer or polymer blend; extruding the melt through a spinneret into filaments; drafting the extruded filaments by means of a suction device at a drafting speed of from 1,000 to 5,000 m/minute, thereby fining them down into finer filaments; depositing such filaments, as they are spread open each other, and are laid up on a travelling collector surface to form a web; and heat-treating the web thereby to obtain the nonwoven fabric.

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## Description

## FIELD OF THE INVENTION

5 The present invention relates generally to filament nonwoven fabrics which are degradable due to microorganisms and the like in natural environments and a method of manufacturing the same. More particularly, the invention relates to a degradable filament nonwoven fabric which can be produced from a polylactic acid-based polymer under particular conditions and a method of manufacturing the same.

## 10 BACKGROUND OF THE INVENTION

Hitherto, nonwoven fabrics which are degradable due to microorganisms have been known including, for example, biodegradable nonwoven fabrics made from natural or regenerated filaments, such as cotton, flax, hemp, ramie, wool, rayon, chitin, and alginic acid filaments.

15 However, such degradable nonwoven fabrics, which are generally hydrophilic and water absorptive, are not suitable for use in such an application as disposable diaper top sheet, wherein it is required that the fabric be hydrophobic and less water absorptive and should have a dry feel when it gets wet. Another problem is that such nonwoven fabrics are very much liable to deterioration in strength and dimensional stability under wet environmental conditions; and this has limited the possibility of exploiting new uses for such nonwoven fabrics in general industrial material applications. Further, such nonwoven fabrics, because of their non-thermoplastic nature, have no thermoformability and are therefore less processable.

20 Recently, therefore, research and development efforts have been positively made for microbially degradable filaments which may be obtainable by the melt spinning technique from a microbially degradable polymer having thermoplastic and hydrophobic characteristics, and microbially degradable nonwoven fabrics made up of such filaments. In particular, a group of polymers generally called aliphatic polyesters are attracting high attention because they have microbial degradation characteristics. Specifically, such polymers include, for example, poly- $\beta$ -hydroxyalkanoate as represented by microbially degradable polyester, poly- $\alpha$ -hydroxyalkanoate as represented by polycaprolactone, poly-alkylene dicarboxylate composed of a polycondensate of glycol and dicarboxylic acid, such as polybutylene succinate, or copolymers of these polymers. In such situation, and with recent development of a new polymerization process which can efficiently produce polymers of high polymerization degree, various attempts have been made to produce filaments from poly- $\alpha$ -oxyacid, a polymeric product as represented by poly-L-lactic acid, and nonwoven fabrics comprised of such filaments. Of aforesaid aliphatic polyesters, polylactic acid in particular has a relatively high melting point such that, when a nonwoven fabric comprised of that material would prove to be very useful in applications which require heat resistance. As such, much expectation is now entertained for possibilities of polylactic nonwoven fabrics for practical use.

35 A polylactic nonwoven fabric is already disclosed in JP-A-7-126970 in which is described a staple filament nonwoven fabric composed principally of polylactic acid. In JP-A-6-212511 there is given a teaching about a polylactic staple filament material useful for the manufacture of polylactic staple filament nonwoven fabrics. However, the manufacture of such a staple filament nonwoven fabric involves many operating stages, from melt spinning and up to nonwoven fabric forming; and this poses a problem from the standpoint of production cost economy.

40 Whilst, in a number of publications, including JP-A-7-48769, JP-A-6-264343, International Nonwovens Journal, Vol. 7, No. 2, pp 69 (1995), and EP 0637641 (A1), suggestions are given for fabrication of filament nonwoven fabrics from polylactic acid under the so-called spun bond technique in which filaments are extruded by melt extrusion for being formed into webs deposited on a screen. However, in JP-A-7-48769, a suggestion is simply given that a nonwoven fabric can be produced from polylactic acid-based polymers by employing the spun bond technique, with no particular mention made as to any specific process for fabrication of such a fabric and the properties of the nonwoven fabric to be obtained. In JP-A-6-264343, which pertains to a biodegradable agricultural filament assembly, there is no detailed statement as to such important manufacturing conditions as filament drafting speed, and other necessary particulars, nor is there any teaching on the properties of the nonwoven fabric produced. The teaching of International Nonwovens Journal, Vol. 7, No. 2, pp 69 (1995) is merely such that hard and brittle plate-like, polylactic spun bonded fabrics were obtained. In EP 0637641 (A1), there is no teaching that a polylactic spun bonded fabric having good flexibility and high mechanical strength can be produced.

## 50 DISCLOSURE OF THE INVENTION

55 The present invention is intended to solve the foregoing problems and has as its primary object the provision of a polylactic filament nonwoven fabric degradable due to microorganisms and the like in natural environments and yet having sufficient mechanical strength for practical use.

In order to accomplish this object, according to the present invention there is provided a nonwoven fabric made up

of filaments comprised of a polylactic acid-based polymer, wherein the polylactic acid-based polymer is a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, said polymer having a melting point of 100° or more, or a blend of such polymers having a melting point of 100°C or more.

In the nonwoven fabric, it is preferable that constituent filaments of the nonwoven fabric are partially bonded with heat and pressure. According to such construction, polylactic acid-based polymer filaments are not joined together at their intersections but are partially bonded with heat and pressure, whereby the nonwoven fabric is allowed to retain its form as such. Therefore, in contrast to known nonwoven fabrics formed with polylactic acid-based polymers, which are characteristically hard and brittle, the nonwoven fabric of the invention has good flexibility while retaining sufficient mechanical strength for practical purposes. Further, being comprised of polylactic acid-based polymer filaments, the nonwoven fabric is well degradable under natural environmental conditions.

In one preferred form of the nonwoven fabric of the present invention, the nonwoven fabric has a areatedly fusion bonded area such that individual filaments at partially preformed temporary bonded areas with heat and pressure are partially separated from one another by a three-dimensionally entangling treatment, and individual filaments at other area than the spottedly fusion bonded area, which is not fusion-bonded, are three-dimensionally entangled together so as to be integrated as a whole. According to such construction, a web preformed with partial temporary bonded areas with heat and pressure has its component filaments three-dimensionally entangled so that the temporarily bonded areas with heat and pressure are at least partially separated, whereby the component filaments, including those at the separated areas, are caused to form three dimensional entanglement, thus enabling the web to retain a nonwoven fabric form. Therefore, in contrast to the known nonwoven fabrics formed with polylactic acid-based polymers, which are characteristically hard and brittle, the nonwoven fabric of the invention has good flexibility while retaining sufficient mechanical strength and dimensional stability for practical purposes.

Further, in the nonwoven fabric of the present invention, it is preferable that individual filaments at partially preformed temporary bonded areas with heat and pressure are completely separated from one another by a three-dimensionally entangling treatment whereby they are three-dimensionally entangled with one another so as to be integrated as a whole.

Further, in the nonwoven fabric of the present invention, it is preferable that at least one side of a web comprised of filaments is bonded with heat and pressure all over. According to such construction, the nonwoven fabric has a filmed surface while internally retaining a nonwoven structure. The filmed surface exhibits good air and water sealing performance and adds much to mechanical strength. This feature is coupled with the existence of the internal nonwoven structure which exhibits good flexibility. As a novel multi-featured nonwoven fabric, therefore, the nonwoven fabric of the invention has a good advantage over sheetings of a complete film form.

According to the present invention, there is also provided a method of fabricating a nonwoven fabric made up of filaments comprised of a polylactic acid-based polymer, comprising the steps of melting a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, said polymer having a melting point of 100° or more, or a blend of such polymers having a melting point of 100°C or more, said polymer or polymer blend having a melt flow rate of 10 to 100 g/10 minutes as measured at 190°C according to ASTM-D-1238 (E), in a temperature range of from (Tm + 20)°C to (Tm + 80)°C, where Tm°C is the melting point of the polymer or polymer blend; extruding the melt through a spinneret into filaments; drafting the extruded filaments by means of a suction device at a drafting speed of from 1,000 to 5,000 m/minute, thereby fining them down into finer filaments; depositing such filaments, as they are spread open each other, and are laid up on a travelling collector surface to form a web; and heat treating the web thereby to obtain the nonwoven fabric.

The invention also presents a nonwoven fabric made up of filaments comprised of a biodegradable polymer composed principally of a thermoplastic aliphatic polyester, wherein the filaments have a crystallization degree of from 7 to 40% and a supercool index of 0.4 or more. A crystallization degree and a supercool index are defined and explained later on.

Further, according to the present invention, there is provided a method of fabricating a nonwoven fabric made up of filaments comprised of a biodegradable polymer composed principally of a thermoplastic aliphatic polyester, which comprises the steps of melting the biodegradable polymer, said biodegradable polymer having a melt flow rate of 10 to 100 g/10 minutes as measured at 190°C according to ASTM-D-1238 (E), in a temperature range of from (Tm + 20)°C to (Tm + 80)°C, where Tm°C is the melting point of the biodegradable polymer; extruding the melt through a spinneret into filaments; drafting the extruded filaments by means of a suction device disposed below the spinneret under a quenching air flow generated through a conventional quenching device at a drafting speed of from 1,000 to 5,000 m/minute, thereby fining them down into finer filaments; then depositing such filaments, as they are spread open each other, and are laid up on a travelling collector surface to form a web; and heat treating the web thereby to obtain the nonwoven fabric.

In this way, the nonwoven fabric in accordance with the present invention is formed from filaments obtained through

the process of rapid filament quenching beneath the spinneret and filament drafting at a drafting speed of from 1,000 to 5,000 m/minute, the filaments having a crystallization degree of from 7 to 40 % and a supercool index of 0.4 or more. This ensures good flow behavior during the process of thermofforming, especially when the thermofforming operation involves complex and acute-angled shaping. Moreover, the nonwoven fabric exhibits less torsion stress and high breaking extension at thermofforming temperatures. This provides an advantage that any breakage which would otherwise possibly occur at times of thermofforming can be effectively prevented. Further, since the nonwoven fabric has a three-dimensional entangled structure, various types of thermofformed products of such a filament nonwoven fabric have a larger specific surface area than thermofformed articles of known sheet materials and can be composted in a very short time. At the same time, this feature enables the filament nonwoven fabric of the invention to find its way into the markets for formed products of which air/liquid permeability is required, as well as those of which fibrous or nonwoven fabric-like hand is required.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 through 6 are illustrations showing, by way of example, different cross-sectional configurations of constituent filaments of nonwoven fabrics in accordance with the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

Filaments employed in the present invention are comprised of a polylactic acid-based polymer.

For the polylactic acid-based polymer is used a polymer having a melting point of 100°C or more selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, the selected polymer having a melting point of 100°C or more, or a blend of such polymers.

Where a homopolymer such as poly(D-lactic acid) or poly(L-lactic acid) is used as a polylactic acid-based polymer, it is desirable that a plasticizer be added thereto especially for enhancement of spinnability during the process of spinning and flexibility improvement with respect to the resulting filaments and nonwoven fabric. Examples of useful plasticizers for such purposes include triacetin, lactic acid oligomers, and dioctyl phthalate. The amount of addition of such a plasticizer should be from 1 to 30 % by weight, preferably from 5 to 20 % by weight.

In the present invention, from the view points of heat resistance and related performance of the nonwoven fabric to be obtained, it is preferable that the melting point of constituent filaments of the nonwoven fabric is 100°C or more. Therefore, it is important that the melting point of the polylactic acid-based polymer, a constituent material of the filaments, be 100°C or more. More specifically, whereas the melting point of poly(L-lactic acid) or poly(D-lactic acid) as a polylactic homopolymer is about 180°C, it is important that, where any of aforesaid copolymers is used as a polylactic acid-based polymer, the copolymerization molar ratio of monomer components must be determined so as to enable the copolymer to have a melting point of 100°C or more. If the copolymerization molar ratio of L-lactic acid or D-lactic acid in the copolymer is lower than a specified range, the melting point of the polylactic polymer is and, in turn, the melting point of constituent filaments of the nonwoven fabric is lower than 100°C, or the polymer may become an amorphous polymer. As such, the quenching effect of filaments in the spinning stage is lowered, and this adversely affects nonwoven fabrics formed from such filaments in respect of heat resistance, with the result that the range of applications for such a nonwoven fabric is limited.

Where the polylactic acid-based polymer is a copolymer of lactic acid and hydroxy-carboxylic acid, examples of hydroxy-carboxylic acid include glycolic acid, hydroxybutanoic acid, hydroxyvaleric acid, hydroxypentanoic acid, hydroxyheptanoic acid, hydroxyoctanoic acid. Of these, hydroxycaproic acid or glycolic acid is particularly preferred from the standpoints of microbial degradation performance and cost economy.

The above enumerated polylactic acid-based polymers may be used alone or in the form of a blend of two or more kinds. In case that such polymers are used in the form of a blend, conditions such as polymers to be mixed and mixing proportions may be suitably determined in consideration of spinnability and other factors.

Such polymers each may be added with various additives, such as dulling agent, pigment, and crystallizing agent, as required within the limits in which the advantageous feature of the invention will not be affected.

The cross section of each constituent filament of the nonwoven fabric may have any cross-sectional configuration, such as solid and otherwise. More specifically, it is preferable that the filament has one of such cross-sectional configurations as hollow section, odd-shaped section, sheath-core type composite section, and slit type composite section.

Fig. 1 shows a cross sectional view in which filament 1 has a hollow cross section. Reference numeral 2 designates a filament portion, and 3 designates a hollow portion. Where a nonwoven fabric is made up of filaments having such a hollow section, the nonwoven fabric has good degradation capability. The reason is that as microorganisms and moisture erode inward from the outer circumferential portion for entry into the hollow portion 3 through holes formed in the filament portion 2 so that the surface area per unit polymer weight is so enlarged as to enhance the rate of degradation by microorganisms and the like. Further, it is significant to note that a filament having an hollow section exhibits good

performance for enhancement of quenching efficiency with respect to filaments spun, because per-unit-time polymer passage through a quenching region during spinning operation is relatively small in weight terms, and because the filament contains therein air bubbles of a small specific heat.

Where the filament has a polygonal odd-shaped cross section or a planar odd-shaped cross section as shown in Figs. 2 and 3, such sectional configuration can enhance filament quenching and spreading-open efficiency in the spinning stage, and can provide improved degradability with respect to the nonwoven fabric to be obtained. The reason for this is that where a filament has an odd-shaped sectional configuration, the filament provides a larger surface area per unit polymer weight.

In case that the filament cross section is a sheath-core type composite section, it is important that after at least one of a polylactic acid-based polymer and a blend of plural kinds of polylactic acid-based polymers is chosen as one filament component, the two kinds of components being arranged in such a manner that one having a higher melting point (hereinafter referred to as high melting point component) is used to assume a core position, the other of a lower melting point (hereinafter referred to as low melting point component) being used to assume a sheath position. In this case, it is also important that between the two components there must be a melting point difference of at least 5°C or more, preferably 10°C or more, more preferably 20°C or more. It is to be noted, however, that where two or more kinds of polylactic acid-based polymer blends are used as core component(s) and/or sheath component(s), the melting point difference between the core and sheath components is determined in such a manner that for the core component, the melting point of one of the constituent polymers of the blend which has a lowermost melting point is taken as a basis, whereas for the sheath component, the melting point of one of the constituent polymers of the blend which has the highest melting point is taken as a basis. Through this arrangement, for the purpose of bonding a web with heat and pressure, it is possible to carry out such bonding operation at a comparatively low temperature, say at a temperature close to the melting point of the sheath component, without causing fusion to the high melting point component of the core portion. Therefore, the resulting nonwoven fabric can have good flexibility.

In case that the filament cross section is a split type composite section, a nonwoven fabric formed from filaments of such a cross-sectional configuration can exhibit good degradability and good flexibility. The term "split type composite section" used herein refers to a filament section such that the filament comprises two kinds of filament components arranged in divisions separate from one another in a circumferential direction of the filament section, the two kinds of filament components including at least one of a polylactic acid-based polymer and a blend of plural kinds of polylactic acid-based polymers, chosen as one filament component, wherein both components extend continuously in the longitudinal direction of the filament and are exposed to the exterior of the filament. Specifically, cross-sectional configurations as shown in Figs. 4 to 6 may be exemplified. More particularly, Fig. 4 shows a cross section wherein two components of filament 1, that is, high melting point component 4 and low melting point component 5 have respective radially extending divisions arranged in alternate relation. Fig. 5 shows a cross section wherein low melting point component 5 constitutes a center portion of filament 1 and wherein high melting point component 4 has a plurality of divisions arranged along a circumferential edge of the low melting point component 5 in such a way that they protrude outward of the low melting point component 5. According to these cross sectional filament configurations, division of the filament itself is accelerated as a portion of a component having higher degradability (usually, low melting point component) is degraded. Therefore, a nonwoven fabric formed from filaments of such cross-sectional configuration will have improved degradability. In Fig. 6, there is shown a filament cross section which is similar to the one shown in Fig. 4 but is different in that there is provided an hollow portion 3. Such filament configuration provides for further improvement in degradability, and filament quenching and spreading-open efficiency. Where such split type composite section is used, it is possible as well to carry out fusion bonding in a temperature range near the melting point of low melting point component 5 during the process of web bonding with heat and pressure. In this operation, no fusion is caused to high melting point component 4. Thus, it is possible to obtain a nonwoven fabric having good flexibility.

In addition to the above described cross-sectional filament configurations, various other odd-shaped composite cross-sectional configurations may be used including, for example, triangular, quadrangular, hexagonal, planar, Y-shaped, and T-shaped.

In the manufacture of the filament nonwoven fabric of the invention, a web is partially bonded with heat and pressure without individual filaments being joined at intersection points, so that the web can retain a sheet-like configuration of nonwoven structure. Such a nonwoven fabric has good flex properties because the constituent filaments are bonded only in partially formed fusion-bonded areas.

In the manufacture of the filament nonwoven fabric of the invention, filaments are previously partially bonded with heat and pressure, whereby filaments are enabled to temporarily retain a web form for purposes of subsequent three-dimensionally entangling. As a result, the nonwoven fabric obtained can have improved shape retention and improved dimensional stability. At such partially effected temporary bonded areas with heat and pressure, filaments are separated entirely or at least partially by a subsequent entangling treatment, so that filaments including the separated filaments can make up a three-dimensional entanglement formation. Thus, the fabric obtained possesses such mechanical strength and dimensional stability as can meet the requirements for practical use. Additionally, the fabric

retains larger parts of non-fusion-bonded areas and can, therefore, also have good flexibility.

The filament nonwoven fabric of the invention may be so constructed that at least one side of the filament-formed web is wholly bonded with heat and pressure so that the fabric can retain a nonwoven fabric conformation. By so constructing, it is possible to provide a nonwoven fabric in which only the surface side of the fabric has a filmed conformation while internally retaining a nonwoven fabric structure. Thus, the nonwoven fabric obtained can, by virtue of the filmed surface configuration, exhibit good air- and water-shielding characteristics and high mechanical strength, and at the same time, by virtue of the internally present nonwoven structure, the nonwoven fabric has far much better flexibility than completely filmed sheet products. Moreover, because of the fact that the filmed surface portion and the interior of nonwoven construction are held in continuous bonding relation, the filament nonwoven fabric of the invention has higher interlayer peel strength than conventional products of the type having a film or films simply laminated on the surface of a nonwoven web.

The single filament fineness of constituent filaments of the nonwoven fabric is preferably in the range of from 1 to 12 denier. If the single filament fineness is less than 1 denier, there may frequently occur single filament breaks in spinning and drafting stages, which results in poor spinning efficiency and lower strength characteristics of nonwoven fabrics obtained. If the fineness is more than 12 denier, quenching effect for filaments spun is insufficient, and the flexibility of filaments obtained is unfavorably affected.

It is preferable that the nonwoven fabric of the invention be comprised of filaments having a single filament fineness of the above mentioned range, and that weight per unit area of the fabric be within the range of from 10 to 200 g/m<sup>2</sup>. If the weight per unit area is less than 10g/m<sup>2</sup>, the fabric has poor texture and insufficient mechanical strength and is unsuitable for practical use. If the weight per unit area is more than 200g/m<sup>2</sup>, the resulting nonwoven fabric is unfavorably affected in flexibility.

The nonwoven fabric of the invention preferably has a tensile strength of not less than 5 kg/5cm width as calculated on the basis of weight per unit area 100 g/m<sup>2</sup>. The term "tensile strength" used herein means an average value of tensile strength measurements in both machine direction which is parallel to the manufacturing line and crossing direction perpendicular to the machine direction as measured according to JIS-L-1096 as will be described hereinafter, which is proportionally converted on the basis of weight per unit area 100 g/m<sup>2</sup> for evaluation. If the tensile strength of the nonwoven fabric is less than 5 kg/5cm width, the mechanical strength of the fabric is too insufficient and may not serve for practical purposes.

Next, the method of fabricating a nonwoven fabric of polylactic acid-based polymer filaments in accordance with the present invention will be explained.

The nonwoven fabric of the invention can be efficiently manufactured by the so-called spun bond process. A polylactic acid-based polymer of the above mentioned type having a melt flow rate of 10-100 g/10 minutes as measured at a temperature of 190°C in accordance with ASTM-D-1238 (E) is melted in a spinning temperature range of from (Tm + 20)°C to (Tm + 80)°C, where Tm°C is the melting point of the polymer, and the melt is spun into filaments through a spinneret which provides a desired filament cross section. The filaments obtained are quenched by means of a conventional quenching device known in the art, such as horizontal blow type or annular blow type, and then the filaments are drafted by a suction device, such as air sucker, in an air stream of from 1,000 to 5,000 m/min. to the desired fineness. Masses of filaments discharged from the suction device are spread open each other and then deposited while being spread open each other on a travelling collector device, such as a screen conveyor, being thus formed into a web. Then, the web formed on the travelling collector device is subjected to heat treatment. A nonwoven fabric is thus obtained.

It is essential that, as earlier stated, the melt flow rate (hereinafter referred to as MFR value) of the polylactic acid-based polymer composition be within the range of 10-100 g/10 min. when measured at 190°C in accordance with the method described in ASTM-D-1238(E). If the MFR value is less than 10 g/10 min., the melting viscosity is excessively high, which results in poor high-speed spinnability. If the MFR value is more than 100 g/10 min., the melting viscosity is too low, which results in poor drafting ability, it being thus difficult to maintain stable operation.

In melt spinning operation, as earlier mentioned, the polymer used should be melted within a temperature range of from (Tm + 20)°C to (Tm + 80)°C, where Tm°C is the melting point of the polymer. However, where a blend of two or more kinds of polylactic acid-based polymers is used, Tm °C should be a melting point which is the highest of the melting points of the constituent polymers of the blend. If the spinning temperature is lower than (Tm + 20) °C, drafting operation in high-speed air currents will be of low efficiency. If the spinning temperature is higher than (Tm + 80) °C, some delay will occur in the process of crystallization at the quenching stage, resulting in inter-filament fusion and poor spreading effect, as well as some thermal decomposition of the polymer itself. Therefore, it is difficult to obtain a nonwoven fabric having good flexibility and uniform texture.

In the process of drafting filaments by means of a suction device to a desired fineness, as already stated, it is important that the drafting speed be within the range of from 1,000 to 5,000 m/min. The drafting speed may be suitably selected according to the MFR value of the polymer. If the drafting speed is less than 1,000 m/min., oriented crystallization of the polymer is retarded, which may result in inter-filament adhesion; and therefore the resulting nonwoven fabric is likely to have hard feel and inferior mechanical strength. If the drafting speed is more than 5,000 m/min., the process of drafting is forced to be carried out in excess of a critical drafting limit, and this results in filament break occur-

rences, it being thus difficult to maintain stable operation.

For heat treatment of webs, a partial bonding apparatus with heat and pressure is used to give partial bonding with heat and pressure at a temperature lower than the melting point which is the lowest of the melting points of polymeric components of the filament. The expression "partially bonding with heat and pressure" means formation of fusion bonded areas by embossing or ultrasonic fusion bonding. Specifically, a web is passed through a clearance between a heated embossing roll and a flat surface metal roll for formation of inter-filament fusion bonded areas.

More particularly, individual bonded areas with heat and pressure, as particular partial areas in a web, each have an area of 0.2 to 15 mm<sup>2</sup> which may be of any configuration, such as circular, elliptic, diamond, triangular, T-shaped, and number sign-shaped. Preferably, the density of distribution of such areas, that is, the density of bonded areas with heat and pressure is within the range of 4 to 100 bonded areas per cm<sup>2</sup>. If the density of bonded areas with heat and pressure is less than 4 bonded areas per cm<sup>2</sup>, no improvement can be had in the mechanical strength and shape retention capability of the resulting nonwoven fabric. If the density is more than 100 bonded areas per cm<sup>2</sup>, the resulting nonwoven fabric is rough and hard and has only poor flexibility. The ratio of total bonded area with heat and pressure to total surface area of the web, that is, pressure bonded area ratio, should be 3 to 50 %, though it depends upon the area of each individual pressure bonded area. If the pressure bonded area ratio is less than 3 %, the resulting nonwoven fabric cannot have improved mechanical strength or improved form retention capability. If the pressure bonded area ratio is more than 50 %, the resulting nonwoven fabric is rough and hard and has only poor flexibility.

Operating temperature for bonding with heat and pressure, that is, the surface temperature of the embossing roll, as already stated, must be lower than the melting point of the polymer used. However, where the web to be bonded with heat and pressure is formed from filaments comprised of a blend of two or more kinds of polyactic acid-based polymers, or where the web is formed from bicomponent filaments having a composite cross-sectional configuration, for example, such a sheath-core type composite section or a split type composite section as earlier mentioned, the melting point of one polymer whose melting point is the lowest of those of all component polymers of the blend, or the melting point of one component of the bicomponent composite cross section which is lower than that of the other is taken as a reference, and operation must be carried out at an operating temperature lower than such a melting point. If the operating temperature exceeds that temperature limit, there may occur polymer adhesion to the bonding apparatus with heat and pressure, with the result that operating efficiency is adversely affected. In addition, the resulting nonwoven fabric has a very hard hand, it being thus impractical to obtain a reasonably flexible nonwoven fabric.

For the operation of bonding with heat and pressure, in addition to the earlier mentioned method using heated embossing rolls, it is possible to adopt a method such that an ultrasonic fusion bonding apparatus is employed to ultrasonically apply a high frequency to the web on a pattern roll, thereby to form inter-filament fusion bonded areas in a pattern section. More specifically, the ultrasonic fusion bonding apparatus comprises an ultrasonic oscillator having a frequency of about 20 kHz which is generally called "horn", and a pattern roll having raised projections arranged circumferentially thereon in a area pattern or belt-like pattern. The pattern roll is disposed below the ultrasonic oscillator so that partial hot fusion bonding can be effected by passing a web through a nip between the ultrasonic oscillator and the pattern roll. Raised projections arranged on the pattern roll may be of a single row or plural rows. In the case of plural-row arrangement, the raised projections may be arranged either in parallel rows or in staggered rows.

Above said operation of partially bonding with heat and pressure using embossing rolls or such an ultrasonic fusion bonding apparatus may be carried out either in a continuous process or in a separate stage. Either way of operation may be suitably selected according to the intended use of the nonwoven fabric.

Next, in the case of a nonwoven fabric of the invention wherein the nonwoven fabric includes area-like fusion bonded areas which are formed as a result of partial separation by a three-dimensionally entangling treatment of individual filaments at previously formed partial temporary bonded areas with heat and pressure, or wherein individual filaments at previously formed partial temporary bonded areas with heat and pressure are already completely separated and individual filaments in non-fusion-bonded areas are three-dimensionally entangled together so that all constituent filaments are integrated as an integral unity, the manufacturing method is as described below.

In this case, a web formed on the travelling deposition apparatus in manner as earlier described is subjected to partial bonding with heat and pressure by a partial bonding apparatus with heat and pressure in an operating temperature range of from (Tm - 80)°C to (Tm - 50)°C, where (Tm)°C represents the melting point of one component polymer which is the lowest of the melting points of all component polymers of the filaments of the web, with linear pressure of a roll set within the range of from 5 to 30 kg/cm, whereby temporary bonded areas with heat and pressure are formed. Next, by effecting a three-dimensionally entangling treatment, individual filaments at temporary bonded areas with heat and pressure at least partially separated so that all constituent filaments including the filaments in separated condition are three-dimensionally entangled into an integral unity. Thus, a filament nonwoven fabric can be obtained.

In this way, by previously effecting partial bonding with heat and pressure, it is possible to permit temporary shape retention so as to enhance the shape retention and mechanical strength of the web for subsequent three-dimensionally entangling operation, thereby facilitating process handling in that operation. Further, since individual filaments at the partial temporary bonded areas with heat and pressure are at least partially separated so that a final nonwoven fabric retains the greater part of its area in non-fusion-bonded condition, it is possible to obtain a nonwoven fabric having good

flexibility. In case that all the individual filaments at partial temporary bonded areas with heat and pressure are completely separated by three-dimensionally entangling treatment, the resulting nonwoven fabric has very good flexibility while retaining its nonwoven configuration in order. Whilst, in case that separation is not completely effected, with temporary heat bonded areas partially left unremoved, three-dimensional entanglement of constituents filaments including separated filaments provides dimensional stability and mechanical strength and, in addition, the fusion bonded areas remaining unremoved serve to provide some reinforcing effect in respect of dimensional stability and mechanical strength.

Aforesaid previously formed partial bonded areas with heat and pressure are preferably such that individual bonded areas with heat and pressure have an area of 0.2 to 15 mm<sup>2</sup>, with the density of fusion bonded areas therein being 4 - 100 bonded areas per cm<sup>2</sup>, preferably 5 - 80 bonded areas per cm<sup>2</sup>. If the density of fusion bonded areas is less than 4 bonded areas per cm<sup>2</sup>, any improvement cannot be obtained in mechanical strength and configurational retention property of the web after heat / pressure bonding. If the density exceeds 100 bonded areas per cm<sup>2</sup>, the processability of the web for three-dimensional entangling treatment is unsatisfactory. The pressure bonded area ratio is 3-50 %, preferably 4-40 %. If the pressure bonded area ratio is less than 3 %, any improvement in dimensional stability cannot be obtained with respect to the resulting nonwoven fabric. Conversely, if the ratio is higher than 50 %, it is likely that the web is less processable for the purpose of three-dimensional entangling.

For bonding operation with heat and pressure, aforesaid conditions of operating temperature and a linear pressure of a roll set are particularly important. If the operating temperature is lower than (Tm - 80)°C and/or if the linear pressure of a roll set is lower than 5 kg/cm, the effect of bonding with heat and pressure is unsatisfactory, and no improvement can be achieved in respect of shape retention performance and dimensional stability of the resulting nonwoven fabric. If the operating temperature is higher than (Tm - 50)°C and/or if the linear pressure of a roll set is higher than 30 kg/cm, the effect of bonding with heat and pressure is excessively large so that individual filaments at the bonded areas with heat and pressure can hardly be partially separated during three-dimensionally entangling operation. Therefore, three-dimensional entanglement of individual filaments in non-fusion-bonded areas cannot sufficiently be effected, it being thus difficult to form all constituent filaments of the web into an integral unity.

By setting conditions of operating temperature and linear pressure of a roll set in such a manner as described above, it is possible to previously form partial temporary bonded areas with heat and pressure within a mass of constituent filaments of the filament web. These partial temporary bonded areas with heat and pressure serve to improve the shape retaining performance and mechanical strength of the web after bonding with heat and pressure and to facilitate process handling during three-dimensional entangling operation. Further, the partial temporary bonded areas with heat and pressure have a certain degree of bonding capability such that individual filaments at such areas can be easily separated at least partially by a mechanical external force applied during the three-dimensionally entangling operation.

The three-dimensional entangling treatment which is given after partial temporary bonding with heat and pressure is carried out through a treatment of pressured liquid stream in which the web is subjected to the action of pressure liquid streams, or through needle punching operation.

Where three-dimensional entangling is carried out through a treatment of pressured liquid stream, a web produced by the earlier mentioned spun bond process, which is formed with partial temporary bonded areas with heat and pressure, is placed on a moving porous support plate and is exposed to the action of pressured liquid streams, whereby individual filaments, including at least partially separated filaments at bonded areas with heat and pressure, are three-dimensionally entangled so that all constituent filaments of the web are integrated as a whole.

To generate pressured liquid streams, an apparatus including an orifice having plural jet holes arranged in one row or plural rows, the jet holes having a bore diameter of from 0.05 to 2.0 mm, preferably from 0.1 to 0.4 mm, adjacent jet holes being 0.3-10 mm spaced apart, is employed. Jet streams of pressured liquid are delivered in a jet pressure range of from 5 to 150 kg/cm<sup>2</sup> G. If the pressure of liquid streams is less than 5 kg/cm<sup>2</sup> G, it is difficult to partially separate bonded areas with heat and pressure. Therefore, entangling of constituent filaments cannot be effected to any sufficient extent. If the pressure is higher than 150 kg/cm<sup>2</sup> G, individual filaments are too densely entangled, and the resulting nonwoven fabric is likely to be less flexible. Jet holes should be arranged in a row along a direction orthogonal to the direction of advance of the web. In case that jet holes are arranged in plural rows, they are preferably arranged in staggered relation from the standpoint of subjecting the web to uniform action of pressured liquid streams. Orifices having jet holes arranged therein may be arranged in plurality. For the pressured liquid, it is common to use fresh water or warm water. The distance between the jet holes and the web should be from 1 to 15 cm. If the distance is less than 1 cm, the texture of the resulting nonwoven fabric is rendered irregular. If the distance is more than 15 cm, the impact force of liquid streams, upon their impingement against the web, is so low that three-dimensional entangling is not sufficiently effected. A support element for supporting the web during pressured liquid treating operation may be, for example, a wire cloth or mesh screen of 10 to 300 mesh, or a porous plate, but is not limited thereto, it being only required that the support element should permit pressured liquid streams to penetrate through the web.

According to the application for which the nonwoven fabric as a final product is to be used, the web subjected to entangling treatment on one side according to the above described method may be turned over and again subjected to entangling treatment by pressured liquid streams. By so doing it is possible to obtain a nonwoven fabric closely inte-



grated on both sides which can exhibit good dimensional stability and high mechanical strength.

After pressured liquid treatment is given, it is necessary that excess moisture be removed from the treated web. For removal of such excess moisture, any known method may be used. For example, it is possible to mechanically remove any residual water to some degree by using a squeezing device, such as mangle roll, and then remove the rest of the water content by employing a drying apparatus, such as continuous hot air drier. Such drying operation may be carried out as ordinary dry heat treatment, but where required, may be carried out as wet heat treatment. For the choice of treating conditions, such as drying temperature and drying time, in carrying out drying operation, conditions may be selected not only for the purpose of moisture removal, but also to allow reasonable degree of shrinkage with respect to the nonwoven web.

Where it is intended to provide three-dimensional entangling by needle punching, a web produced according to the spun bond process, with partial temporary bonded areas with heat and pressure formed thereon, is punched through by punch needles so that filaments including at least partially separated filaments at those areas bonded with heat and pressure are three-dimensionally entangled for integration as a whole.

Needle punching is preferably carried out under the conditions of; needle depth, 5-50 mm; punching density, 50-400 punches/cm<sup>2</sup>. If the needle depth is less than 5 mm, the degree of entanglement of filaments is insufficient, which in turn results in poor dimensional stability, while a needle depth of more than 50 mm poses a problem from the standpoint of productivity. If the punch density is less than 50 punches/cm<sup>2</sup>, constituent filaments at bonded areas with heat and pressure may not be smoothly separated and entangling of filaments may not sufficiently be effected; and the resulting nonwoven fabric may lack dimensional stability. If the punch density is more than 400 punches/cm<sup>2</sup>, filament breaks due to punch needles may occur and the resulting nonwoven fabric may be of lower mechanical strength. Punch needles are selectable in respect of thickness, length, number of barbs, barb pattern, etc. according to the single filament fineness, intended use, etc.

Aforesaid pressured liquid stream treatment is applicable to products of lower weight per unit area (15 - 200 g/m<sup>2</sup>), and by such treatment it is possible to obtain nonwoven fabrics having good flexibility and high mechanical strength. Needle punch treatment is applicable to products of higher weight per unit area (100 - 500 g/m<sup>2</sup>), and by such treatment it is possible to obtain having good flexibility, good air permeability, and good water permeability. The reason for selection of applicable treatment according to the weight per unit area is that there is some difference in web penetration capability between pressured liquid streams and needle punches. For example, when a pressured liquid stream treatment is applied to articles of higher weight per unit area, pressured liquid streams do not penetrate through the web in the direction of web thickness; therefore, entangling of filaments is effected only with respect to the surface layer of the web, no uniform three-dimensional entanglement being formed over the entire web. Therefore, it is desirable that which one of the treatment methods is to be selected should be determined according to the weight per unit area of the nonwoven fabric and the purpose for which the nonwoven fabric is to be used.

When selection is made in this way, at fusion bonded areas which have been destroyed through three-dimensionally entangling treatment and still remain as such to some degree, the pressured bonded area density is 20 bonded areas per cm<sup>2</sup> or less, preferably 10 bonded areas per cm<sup>2</sup> or less, and the pressure bonded area ratio is 15 % or less, preferably 10 % or less. A filament nonwoven fabric having such fusion bonded areas can take advantage of the presence of non-fusion-bonded areas to effectively provide filament to filament entangling through the three-dimensionally entangling treatment. Thus, the nonwoven fabric can exhibit good dimensional stability and high mechanical strength. In case that fusion bonded areas partially remain in existence, such fusion bonded areas adds to the dimensional stability and mechanical strength of the nonwoven fabric. Further, as earlier mentioned, temporary bonded areas with heat and pressure are separated in part or wholly by three-dimensionally entangling treatment, and this in effect means the presence of a large non-fusion-bonded area, which enables the fabric to exhibit good flexibility, while in non-fusion-bonded region, filaments are three-dimensionally entangled, which adds to dimensional stability and mechanical strength.

Next, the method of fabricating a nonwoven fabric of the invention, wherein at least one side of the web comprised of filaments is bonded with heat and pressure all over, will be explained.

Prior to such overall bonding with heat and pressure, a web formed on the travelling deposition apparatus may be subjected to partial temporary bonding with heat and pressure as required. Also, after the partial temporary bonding with heat and pressure, it is possible to effect three-dimensionally-entangling treatment for bulkiness improvement. The purpose of aforesaid partial temporary bonding is to prevent troublesome web-to-web entangling that may possibly occur when webs successively formed in the spun bond process are tentatively wound, which may in turn make it difficult to unwind the web roll. Therefore, the partial temporary bonding with heat and pressure to be effected for such purpose may be of such a tentative form retentive nature as to prevent entangling at the time of winding.

Overall bonding of webs with heat and pressure is carried out by melting the web surface and adjacent filaments by means of a heated metal roll having a smooth surface to cause the web surface to be turned into a film form.

As earlier stated, the operating temperature for overall bonding with heat and pressure, that is, the surface temperature of the metal roll must be a temperature lower than  $(T_m + 10)^\circ\text{C}$ , where  $T_m^\circ\text{C}$  is the melting temperature of the polymer used.

However, where the web to be bonded with heat and pressure is formed from filaments comprised of a blend of two or more kinds of polylactic acid-based polymers, or where the web is formed from bicomponent filaments having a composite cross-sectional configuration, for example, such a sheath-core type composite section or a split type composite cross section as earlier mentioned, the melting point of one polymer whose melting point is the lowest of those of all component polymers of the blend, or the melting point of one component of the bicomponent composite section which is lower than that of the other is taken as a reference. If the operating temperature exceeds that temperature limit, there may occur polymer adhesion to the bonding apparatus with heat and pressure, with the result that operating efficiency is adversely affected. In addition, the resulting nonwoven fabric has a very hard hand and poor texture.

For the purpose of bonding with heat and pressure, it is important that linear pressure of a roll set should be 0.01 kg/cm or more. If the linear pressure of a roll set is less than 0.01 kg/cm, the effect of bonding with heat and pressure is insufficient, and the resulting nonwoven fabric will not exhibit improved mechanical strength, nor will it exhibit improved dimensional stability. Whilst, if the linear pressure of a roll set is more than 10 kg/cm, the effect of bonding with heat and pressure is excessive so that the resulting nonwoven fabric as a whole will have a film-like structure, the nonwoven fabric being of no more than a hard and rough structure. Preferably, therefore, the linear pressure of a roll set should be not more than 10 kg/cm.

In the present invention, a web should be bonded with heat and pressure at least on one side. Where the web is bonded with heat and pressure on both sides, in particular, the resulting nonwoven fabric comprises a three-layer structure such that film layers having air-and-water shielding properties are disposed at both surfaces, and a air-containing nonwoven fabric layer placed between the film layers. In this case, a nonwoven fabric having good heat retaining properties can be obtained.

Bonding with heat and pressure may be carried out in a continuous operation process or as a separate stage of operation.

In one aspect of the invention, as earlier stated, a nonwoven fabric of the invention is comprised of filaments spun from a biodegradable polymer composed principally of a thermoplastic aliphatic polyester, the filaments having a crystallization degree of from 7 to 40 % and a supercool index of 0.4 or more.

According to the present invention, a method of fabricating a nonwoven fabric made up of filaments comprised of a biodegradable polymer composed principally of a thermoplastic aliphatic polyester comprises the steps of melting the biodegradable polymer, said biodegradable polymer having a melt flow rate of from 10 to 100 g/10 minutes as measured at 190°C according to ASTM-D-1238 (E), in a temperature range of from  $(T_m + 20^\circ\text{C})$  to  $(T_m + 80^\circ\text{C})$ , where  $T_m$  is the melting point of the biodegradable polymer; extruding the melt through a spinneret into filaments; drafting the extruded filaments by means of a suction device disposed below the spinneret under a quenching air blow generated through a conventional quenching device and at a drafting speed of from 1,000 to 5,000 m/minute, thereby fining them down into finer filaments; then depositing such filaments, as they are spread open each other, and are laid up on a travelling collector surface to form a web; and heat-treating the web thereby to obtain the nonwoven fabric.

As stated above, filaments used in the invention are formed from a biodegradable polymer composed principally of a thermoplastic aliphatic polyester.

Examples of thermoplastic aliphatic polyesters include poly( $\alpha$ -hydroxy acid), such as polyglycolic acid or polylactic acid, and copolymers of repeating units mentioned above or constituents of such polymers. Also enumerated as such are poly( $\epsilon$ -caprolactone), poly( $\omega$ -hydroxyalkanoate) such as poly( $\beta$ -propiolactone), poly-3-hydroxypropionate, poly-3-hydroxybutyrate, poly-3-hydroxycaprolate, poly-3-hydroxyheptanoate, poly( $\beta$ -hydroxyalkanoate) such as poly-3-hydroxyoctanoate, and copolymers of the repeating units mentioned above or constituents of these polymers and the repeating units mentioned above or constituents of poly-3-hydroxyvalerate or poly-4-hydroxybutyrate. Also, polycondensates of glycol and dicarboxylic acid may be mentioned as such, including, for example, polyethylene oxalate, polyethylene succinate, polyethylene adipate, polyethylene azelate, polybutylene oxalate, polybutylene succinate, polybutylene adipate, polybutylene sebacate, polyhexamethylene sebacate, polyneopentyl oxalate, and polyalkylene dicarboxylate copolymer comprising any of these as repeating units.

In the present invention, of the above enumerated, polylactic acid-based polymer, any one of polybutylene succinate, polyethylene succinate, polybutylene adipate, and polybutylene sebacate, or copolymers in which these polymers are included as repeating units, one of polycaprolactone and polypropiolactone, or copolymers in which these polymers are included as repeating units, are preferred from the standpoints of biodegradability, spinnability or the like.

In case that the aliphatic polyester is a polylactic acid-based polymer, specifically, any one of poly(D-lactic acid), poly(L-lactic acid), copolymer of D-lactic acid and L-lactic acid, copolymer of D-lactic acid and hydroxycarboxylic acid, and copolymer of L-lactic acid and hydroxycarboxylic acid which has a melting point of 100°C or more is preferred. In a copolymer of lactic acid and hydroxycarboxylic acid, the hydroxy-carboxylic acid may be, for example, glycolic acid, hydroxybutyric acid, hydroxyvaleric acid, hydroxypentanoic acid, hydroxycaproic acid, hydroxyheptanoic acid, or hydroxyoctanoic acid. In this case, in order that the nonwoven fabric, as a product, may possess good formability, the number-average molecular weight of the polylactic acid-based polymer is preferably 50,000 - 95,000.

In the case where aliphatic polyester is polyalkylene dicarboxylate, any polymer selected from the group consisting of polybutylene succinate, polyethylene succinate, polybutylene adipate, and polybutylene sebacate, or a copolymer in

which such polymers are included as repeating units, is preferred as such. Specifically, a copolymer of not less than 70 mol % of butylene succinate and one of ethylene succinate, butylene adipate, and butylene sebacate is preferred.

Such biodegradable polymers as above enumerated may be used in a blend of plural selected polymers.

Further, it is possible to use, as a biodegradable polymer, a polycondensed product of aforesaid thermoplastic aliphatic polyester and aliphatic polyamide, such as polycapramide (nylon 6), polytetramethylene adipamide (nylon 46), polyhexamethylene adipamide (nylon 66), polyundecanamide (nylon 11), and polytauramide (nylon 12), that is, an aliphatic polyester amide-based copolymer.

From the standpoints of spinability and resulting filament property, it is desirable that such biodegradable polymer should have a number-average molecular weight of not less than about 20,000, preferably not less than 40,000, more preferably not less than 60,000. Polymers which are chain-extended with a small amount of diisocyanate or tetracarboxylic dianhydride to enhance polymerization degree may also be used.

The biodegradable polymer may be added with various kinds of additives, such as dulling agent, pigment, and crystallizing agent, as required, but within the limits which are not detrimental to the intended effects. In particular, addition of crystallizing agents, such as talc, boron nitride, calcium carbonate, magnesium carbonate, and titanium oxide is desirable, because it can prevent inter-filament blocking at spinning and quenching stages, and because it can enhance crystallization during thermoforming operation and improve heat resistance and mechanical strength characteristics. However, since excessive promotion of filament crystallization will affect formability characteristics, the amount of such addition is within the range of from 0.1 to 3.0 wt %, more preferably from 0.5 - 2.0 wt %.

The filament configuration of constituent filaments of the nonwoven fabric may be solely of aliphatic polyester or may be of a composite of two or more kinds of aliphatic polyesters. The filament cross section of constituent filaments may be a usual circular section, an irregular section, an hollow section, or a composite section such as sheath-core type section.

The single filament fineness of constituent filaments of the nonwoven fabric is preferably 20 denier or less, more preferably 1 to 12 denier. If the fineness is more than 20 denier, filament quenching at the spinning stage is hindered, and in addition the flexibility characteristics of the resulting nonwoven fabric are unfavorably affected. This is inconvenient from the standpoint of thermoforming operation with the nonwoven fabric, because the fabric does not allow smooth working especially when some complex and acute-angled deformation work is involved.

The weight per unit area of the nonwoven fabric, as a commercial product, is preferably within the range of 10 to 500 g/m<sup>2</sup>. If the weight per unit area is less than 10 g/m<sup>2</sup>, the nonwoven fabric is of poor appearance and insufficient in mechanical strength, being unsatisfactory for practical use. If the weight per unit area is more than 500 g/m<sup>2</sup>, flexibility is affected. Where finer single filament is involved, the fabric is of greater denseness than a nonwoven fabric of the same weight per unit area which is made up of filaments of coarser single filament. However, the fact that deterioration in mechanical strength due to biodegradation is faster must be taken into consideration. Where the mechanical strength of the filament itself is low, a larger weight per unit area is required in order to enable the fabric to maintain a certain degree of strength.

Constituent filaments of the nonwoven fabric of the invention should have a crystallization range of from 7 to 40 % and a supercool index of 0.4 or more. This is basic requirements for affording efficient working during thermoforming operation, especially at the time of complex and acute angle deformation work.

A crystallization degree is determined from a wide-angle X-ray diffraction pattern of powdered filament according to the Ruland method. Whilst, a supercool index is expressed by an equation based on a fusion endotherm curve (heat up/melting and heat down), details of which will be described hereinafter. These are reference indices as to formability. Where a crystallization degree is less than 7 %, fusion breakage is likely to occur at a high deformation region. If a crystallization degree is more than 40 %, heat deformation is less likely to occur, which makes it difficult to carry out high drafting forming. Where a supercool index is less than 0.4, the nonwoven fabric lacks transformation ability during thermoforming operation.

The above mentioned requirements being met by constituent filaments of the nonwoven fabric means that the nonwoven fabric is acceptable for thermoforming operation with it. This in turn means that strain-stress is low at the thermoforming temperature and elongation at break is high. Therefore, the nonwoven fabric can be prevented from breaking during thermoforming operation. For example, elongation at break of the nonwoven fabric is 20 % or more, preferably 30 % or more, more preferably, 40 % or more.

Another basic requirement is that the filament nonwoven fabric and constituent filaments thereof are not liable to shrink during thermoforming operation. The reason is that if any shrinking of the web sheet occurs at the time of forming, the sheet is taken up by the mold, which prevents stable continuous forming operation. Therefore, the shrinked area of the nonwoven fabric at the time of thermoforming operation is not more than 10%, preferably not more than 5 %, more preferably not more than 2 %.

The nonwoven fabric of the invention maintains a sheet-form configuration having a nonwoven structure because of the fact that the web is subjected to heat treatment.

One configurational feature of the nonwoven fabric of the invention is that the web is partially bonded with heat and pressure. The nonwoven fabric of such configuration in accordance of the invention has good flexibility performance,

because the fabric is bonded only at the fusion bonded areas. This provides for maintenance of smooth working capability during thermoforming operation, especially at the time of complex and acute-angled deformation work, and also provides for improvement in the form retention capability of the nonwoven fabric during thermoforming operation.

Another configurational feature of the nonwoven fabric of the invention is such that the fabric has fusion bonded areas formed when individual filaments at preformed partial temporary bonded areas with heat and pressure were partially separated through three-dimensional entangling treatment, and such that individual filaments at non-fusion-bonded portions in areas other than the fusion bonded areas are three-dimensionally entangled so that the fabric is integrated as a whole.

A still another configurational feature of the nonwoven fabric of the invention is such that individual filaments at preformed partial temporary bonded areas with heat and pressure are completely separated and three-dimensionally entangled through three-dimensional entangling treatment and are integrated as a whole.

A further configurational feature of the invention is such that at least one side of the web comprised of filaments is bonded with heat and pressure all over.

Details of these configurations are same as those already described and are not repeated herein.

Next, method of manufacturing above described nonwoven fabric will be explained in detail.

As earlier described, a biodegradable polymer must have an MFR value measured according to the method stated in ASTM-D-1238 (E) which is within the range of 10 - 100 g/10 min. If the MFR value is less than 10 g/10 min., the melt viscosity is too high and therefore the efficiency of drafting by air sucker or the like is poor, which may be a cause of filament break at the spinning stage. If the MFR value is more than 100 g/10 min., the melt viscosity is too low, which leads to poor drafting efficiency, it being thus difficult to carry out operation in stable condition.

Spinning temperature should be suitably selected by taking into consideration the type of polymer, MFR value of the polymer, or the like. If the spinning temperature is too low, the result is poor drafting efficiency. If the spinning temperature is too high, interfilament adhesion may be caused, resulting in poor filament-spreading-out effect; and in addition, thermal decomposition of the polymer itself will proceed.

During spinning operation, filaments just after being spun are subjected to quenching air blow at more than a certain rate with care not to cause any substantial filament shaking. The suction device is preferably set at a location below and at 1 to 2 m distance from the spinneret. Where necessary, earlier mentioned crystallizing agent may be added to enhance quenching effect.

For the purpose of drafting and thinning filaments spun by means of the suction device, as earlier mentioned, it is important that the drafting speed be within the range of 1,000 to 5,000 m/min. Through such arrangement, it is possible to achieve a crystallization degree of from 7 to 40 % with respect to constituent filaments of the nonwoven fabric and a supercool index of 0.4 or more. If the drafting speed is less than 1,000 m/min., crystallization of oriented polymers will not progress so that the crystallization degree of filaments may be less than 7 %, thus resulting in lower mechanical strength of the resulting nonwoven fabric. If the drafting speed is more than 5,000 m/min., crystallization of oriented polymers will progress excessively so that the crystallization degree of filaments may exceed 40 % and, in addition, the supercool index may be lower than 0.4. As a result, the filaments are subject to higher strain-stress at thermal deformation temperatures, which leads to poor thermoformability. Therefore, it is especially preferable that the drafting speed be 1,200 to 3,000 m/min.

For heat treatment of web, it is possible to use partial bonding with heat and pressure which creates fusion bonded areas by embossing treatment or ultrasonic fusion bonding treatment. In this case, the operating temperature for bonding with heat and pressure, that is, the surface temperature of the embossing roll is preferably lower than the melting point of one polymer having lowest melting point in case that the web is comprised of plural kinds of polymers. If the operating temperature exceeds this temperature, polymer adhesion to the bonding apparatus with heat and pressure may occur, which adversely affects operating efficiency. Moreover, the resulting nonwoven fabric feels hard and is less adaptable to a mold having a complex configuration, leading to poor formability.

Pressure bonded area ratio for bonding with heat and pressure may be from 3 to 50 %. If this ratio is less than 3 %, the resulting fabric will have poor form retention property necessary for fabric handling purposes and poor dimensional stability. If this ratio is more than 50 %, the resulting nonwoven fabric feels hard and is less adaptable to a mold having a complex configuration, leading to poor formability.

This partial bonding with heat and pressure may be carried out in a continuous process operation or in a separate operation stage. The choice of either method may be determined suitably, for example, according to the formed product to be manufactured using the nonwoven fabric obtained.

Other details of this partial bonding with heat and pressure are as already described. For example, two or more kinds of components comprised of biodegradable polymers are melt spun through a spinneret which provides a composite filament cross section, and partial bonding with heat and pressure is carried out at a temperature lower than the melting point of the polymer which is the lowest in melting point of the two or more kinds of polymers.

Another method for heat treatment of webs is such that temporary bonded areas with heat and pressure are formed by applying a partial bonding treatment with heat and pressure to the web; then individual filaments at the temporary bonded areas with heat and pressure are partially separated by effecting three-dimensional entangling treatment; then

individual filaments in separated state are three-dimensionally entangled into overall integration.

In that case, a partial bonding operation with heat and pressure for forming temporary bonded areas with heat and pressure is carried out by pressing the web by means of the embossing roll. For this purpose, it is important that such bonding operation is carried out at an operating temperature of from  $(T_m - 80)^\circ\text{C}$  to  $(T_m - 50)^\circ\text{C}$ , where  $T_m^\circ\text{C}$  is the melting point of the polymer having the lowest melting point of the component polymers, with the linear pressure of a roll set at 10 - 100 kg/cm. The reason for this is as already stated.

Other details of the three-dimensional entangling treatment are as already stated.

As another method for web heat treatment, it is possible to bond at least one side of the web with heat and pressure.

In that case, the treatment for overall bonding with heat and pressure is carried out by means of calender roll or Yankee drier at a temperature lower than  $(T_m + 10)^\circ\text{C}$ , where  $T_m^\circ\text{C}$  is the melting point of the biodegradable polymer, with the linear pressure of the roll set at 0.01 kg/cm or more. The reason is as earlier mentioned.

In that case, the web which is formed by causing filaments to be deposited, while being spread open, on the travelling collector surface is subjected to partial temporary bonding with heat and pressure. Subsequently, at least one side of the web is bonded with heat and pressure all over.

Two or more kinds of components comprised of biodegradable polymers may be melt spun through a spinneret which provides for a composite cross section configuration, and at least one side may be bonded with heat and pressure all over at a temperature lower than  $(T_m + 10)^\circ\text{C}$ , where  $T_m^\circ\text{C}$  is the melting point of one polymer which is the highest melting temperature of the two or more components.

Other details of the overall bonding with heat and pressure are as earlier stated.

As already stated, it is possible to carry out thermoforming operation using the biodegradable filament nonwoven fabric as a material. In this case, if the component polymer of the nonwoven fabric, or the nonwoven fabric are comprised of plural polymers, one polymer having the highest melting point of the polymers is taken as a subject polymer, and the nonwoven fabric is preheated at a temperature higher than the glass transition temperature of, but lower than the melting point of the subject polymer, being then subjected to pressed forming in a mold. Thereafter, for improving the mechanical strength of the resulting formed piece, crystallization is enhanced at temperatures in the vicinity of the crystallizing temperature.

#### EXAMPLES

The invention will be explained more specifically with reference to the following examples. It is understood, however, the invention is in no way limited to these examples.

In the following examples and comparative examples, various property values were determined as stated below.

MFR (Melt Flow Rate) value (g/10 min.): measured at  $190^\circ\text{C}$  in accordance with the method described in ASTM-

D-1238 (E).

Melting point ( $^\circ\text{C}$ ) and supercool index: In a fusion-endotherm curve based on measurements obtained by means of a differential scanning calorimeter, Model DSC-2 made by Perkin Elmer, with a sample weight of 5 mg, and the rate of temperature rise set at  $20^\circ\text{C}/\text{min}$ , an intermediate temperature between a shift start temperature at the base line and a shift end temperature was determined to be a glass transition temperature  $T_g$  ( $^\circ\text{C}$ ), and a temperature which gives the extreme of endothermic peaks was determined to be a melting point  $T_m$  ( $^\circ\text{C}$ ). Then, after the sample was maintained in melted condition for 10 minutes, quenching was effected at a temperature decreasing rate of  $20^\circ\text{C}/\text{min}$ . In an exotherm curve obtained, a temperature which gives a maximum value was determined to be a crystallizing temperature  $T_c$  ( $^\circ\text{C}$ ). Where two or more maximum values were given, a main peak was adopted as the maximum value. Supercool index was determined according to the following relation.

$$\text{Supercool index} = (T_m - T_c) / (T_m - T_g)$$

Weight per unit area ( $\text{g}/\text{m}^2$ ): From each sample in standard condition were prepared 10 specimens, each of 10 cm x 10 cm. After the moisture content of each specimen was brought to equilibrium, each specimen was weighed for determining the weight (g) thereof. The average of the values obtained was converted into a value per unit area, which was defined as weight per unit area ( $\text{g}/\text{m}^2$ ).

KGSM tensile strength ( $\text{kg}/5 \text{ cm width}$ ) Measurement was made in accordance with the strip method described in JIS-L-1096. Ten specimens, each being 5 cm wide and 20 cm long, were prepared for each sample, and by using a constant stretch type tensile strength tester ("Tension UTM-4-1-100", made by Toyo Baldwin), each specimen was stretched by being clamped at positions 10 cm distanced from each other, at a stretch rate of 10 cm/min in both directions of the nonwoven fabric, i.e., machine direction which is parallel to the manufacturing line and crossing direction perpendicular to the machine direction. The average of breaking load values ( $\text{kg}/5 \text{ cm width}$ ) obtained was converted on a  $100 \text{ g}/\text{m}^2$  weight per unit area basis, and the converted value was taken as a KGSM tensile strength ( $\text{kg}/5 \text{ cm width}$ ).

Biodegradability: Nonwoven fabrics were buried in an aged compost maintained at about 58°C and were taken out three months later. In the case where the nonwoven fabric did not retain its configuration as such, or where even if the fabric retained its configuration, its tensile strength had been lowered to 50 % or less of the initial strength level of the fabric prior to the burial, the degradability of the nonwoven fabric was evaluated to be good, whereas in case that the strength was more than 50 % of the initial strength prior to the burial, the nonwoven fabric was evaluated to be of poor degradability.

Filament crystallization degree (%): Measured according to a wide-angle X-ray diffraction method (powdered; Ruland Method). In the wide-angle X-ray diffraction method, diffracted X-ray interference intensity measurements were made in the direction of reflection angle  $2\theta$ , whereby an diffracted intensity curve was obtained. Then, from the diffracted intensity curve were separated to a crystal-based diffracted peak and an amorphous portion-based dispersion halo, which were quantitatively determined. Thus, crystallization degree was calculated from the following relation.

Crystallization degree (%) = (crystal portion integral diffracted intensities / total integral diffracted intensities)  $\times$  100.

Air permeability ( $\text{cc} / \text{cm}^2 / \text{sec.}$ ): Measured according to the Frazir type method described in JIS-L-1096. More specifically, 3 specimens, each of 15 cm in length and 15 cm in width, were prepared. A Frazir type tester was used in such a way that, after a specimen was attached to one end of a cylinder, a suction pump adjustment was made by means of a variable resistor so as to allow an inclined type barometer to give a pressure reading of 12.7 mmH<sub>2</sub>O. Then, the quantity of air passing through the specimen ( $\text{cc}/\text{cm}^2/\text{sec.}$ ) was determined on the basis of pressure readings of a vertical type barometer and according to the type of air spouting orifice used. Average value with respect to three specimens was taken as air permeability.

#### Example 1

An L-lactic acid-hydroxycaproic acid copolymer of L-lactic acid / hydroxycaproic acid = 90 / 10 mol % which has a melting point of 168 °C and an MFR value of 20 g/10 min. was melt spun into filaments through a circular spinneret at a spinning temperature of 195°C and at a mass out flow rate from each orifice of 1.75 g/min. The filaments were quenched by a conventional quenching device, and were then drafted and attenuated at a drafting speed of 4500 m/min. Filaments were spread open each other and deposited on a collecting surface of a travelling conveyor, being thus formed into a web. The web was then passed through a partial bonding apparatus with heat and pressure comprising embossing rolls wherein partial bonding with heat and pressure was carried out under the following conditions: roll temperature of 138°C, or 30°C lower than the melting temperature of the polymer; pressure bonded area ratio of 15.0 %; pressure bond density of 22.0 bonded areas per  $\text{cm}^2$ ; and linear pressure of a roll set of 50 kg/cm. Thus, a filament nonwoven fabric comprised of filaments of 3.5 denier in single filament fineness and having a weight per unit area of 30 g/m<sup>2</sup> was obtained. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this instance are shown in Table 1.

TABLE 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Polymer	MPR value	20	20	20	20	20	20	20	20
	D-lactic acid copolymerization ratio	0	0	80	20	0	0	0	10
	L-lactic acid copolymerization ratio	90	70	20	80	100	Note 1	90	80
	Hydroxyproprionic acid copolymerization ratio	10	30	0	0	0	0	10	20
	Melting point	168	139	110	112	178	178	188	141
Manufacturing conditions	Filament cross section	—	Solid	Solid	Solid	Solid	Solid	Solid	Divided type composite (Fig. 5)
	Spinning temperature	195	165	135	135	200	200	195	170
	Single-hole discharge rate	1.75	1.35	1.24	1.24	1.79	1.67	3.00	1.59
	Drafting speed	4500	3500	3200	3200	4600	4300	5000	4100
	Balloss temperature	138	110	80	82	148	148	138	81
Operational performance	Adhesion	—	None	None	None	None	None	None	None
	Filament break	—	None	None	None	None	None	None	None
	Filament spreading-open efficiency	—	Good	Good	Good	Good	Good	Good	Good
	Single filament fineness	Denier	3.5	3.5	3.5	3.5	3.5	3.4	3.5
	Weight per unit area	g/m <sup>2</sup>	30	30	30	30	30	30	30
Nonwoven fabric properties	WCSN strength	kg/cm width	14	11	13	12	16	17	14
	Texture	—	Good	Good	Good	Good	Good	Good	Good
	Biodegradability	—	Good	Good	Good	Good	Good	Good	Good

Note 1: L-lactic acid polymer was added with 1 wt% talc as crystallizing agent.

Note 2: Glycolic acid was used in place of hydroxyproprionic acid.

## Example 2

The copolymerization ratio of L-lactic acid to hydroxycaproic acid in the L-lactic acid-hydroxycaproic acid copolymer, and the spinning temperature, the mass out flow rate, the drafting speed, and the embossing temperature were changed as shown in Table 1. In other respects, operation was carried out in the same way as in Example 1 to obtain a filament nonwoven fabric. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained in this Example 2 are shown in Table 1.

## Examples 3 and 4

A filament nonwoven fabric was produced using a copolymer of L-lactic acid and D-lactic acid. The copolymerization ratio of L-lactic acid to D-lactic acid, spinning temperature, mass out flow rate, drafting speed, and embossing temperature used in each respective example were as shown in Table 1. In other respects, operation was carried out in the same way as in Example 1 to obtain the nonwoven fabric. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained, in each respective Example 3, 4 are shown in Table 1.

## Example 5

A filament nonwoven fabric was produced using poly(L-lactic acid). The spinning temperature, mass out flow rate, drafting speed, and embossing temperature used in this Example 5 were as shown in Table 1. In other respects, operation was carried out in the same way as in Example 1 to obtain the nonwoven fabric. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained are shown in Table 1.

## Example 6

A filament nonwoven fabric was produced using a composition comprising poly(L-lactic acid) and 1 wt % of talc added thereto as a crystallizing agent. The mass out flow rate and drafting speed used in this Example 6 were as shown in Table 1. In other respects, operation was carried out in the same way as in Example 5 to obtain the filament nonwoven fabric. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained are shown in Table 1.

## Example 7

Operation was carried out in the same way as in Example 1, except that a mass out flow rate of 3.00 g/min. and a drafting speed of 5,000 m/min. were used. As a result, a filament nonwoven fabric comprised of filaments having a single filament fineness of 5.4 denier was obtained. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained in this Example 7 are shown in Table 1.

## Example 8

A copolymer of L-lactic acid / glycolic acid = 80 / 20 mol % having a melting point of 111 °C and an MFR value of 20 g/10 min. was used as a first component, and a poly (D, L-lactic acid) of L-lactic acid / D-lactic acid = 90 / 10 mol % having a melting point of 141°C and an MFR value of 20 g / 10 min. as a second component. The two components were used in the following ratio: the first component / the second component = 1 / 1 (weight ratio). The components were melt spun into filaments through a spinneret having a configuration such that, in a split type composite cross section as shown in Fig. 5, the first and second components could be respectively arranged in the core and leaf portions, the spinning operation being carried out at a spinning temperature of 170°C and at a mass out flow rate of 1.59 g/min. Filaments spun were quenched by a conventional quenching device and were then drafted and attenuated at a drafting speed of 4,100 m/min. Filaments were spread open each other and deposited on a collecting surface of a travelling conveyor, being thus formed into a web. The web was then passed through a partial bonding apparatus with heat and pressure comprising embossing rolls having a circular protrusion of 3.1 mm<sup>2</sup> in area wherein partial bonding with heat and pressure was carried out under the following conditions: roll temperature of 81°C; pressure bonded area ratio of 6.1%; pressure bond density of 6.7 bonded areas per cm<sup>2</sup>; and linear roll pressure of 40 kg/cm. As a result, a split type composite filament nonwoven fabric comprised of filaments of 3.5 denier in single filament fineness (fineness of each leaf segment: about 0.3 denier) and having a weight per unit area of 30 g/m<sup>2</sup> was obtained. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 8 are shown in Table 1.

As is apparent from Table 1, all the filament nonwoven fabrics obtained in Examples 1 through 8 had sufficient strength to enable the fabric to serve for practical purposes. The nonwoven fabrics also had very good biodegradability such that when removed from a compost in which these nonwoven fabrics had been buried, and all the fabrics were



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found as having undergone considerable decrease in weight, substantial changes in configuration, and considerable degradation in strength maintenance.

## Comparative Examples 1 and 2

Filament nonwoven fabrics were produced in the same way as in Example 1, except that the drafting speed was changed as shown in Table 2. Manufacturing conditions and spinnability in these comparative examples are shown in Table 2.

TABLE 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
Polymer	MFR value	20	20	150	0.6	20	20	20
	D-lactic acid copolymerization ratio	0	0	0	0	0	0	20
	L-lactic acid copolymerization ratio	90	90	90	90	90	90	80
	Hydroxyacrylic acid copolymerization ratio	10	10	10	10	10	10	0
	Melting point	168	168	168	168	168	168	112
Manufacturing conditions	Filament cross section	—	Solid	Solid	Solid	Solid	Solid	Solid
	Spinning temperature	185	185	185	185	180	270	125
	Single-hole discharge rate	1.75	1.75	1.75	1.75	1.75	1.75	1.24
	Drafting speed	800	6500	4500	4500	4500	4500	3200
	Emboss temperature	—	—	—	—	—	—	113
Operational performance	Adhesion	—	Present	None	None	None	Present	None
	Filament break	—	None	Present	Present	Present	Present	None
	Filament Spreading-open efficiency	—	Poor	—	—	—	—	Good
Nonwoven fabric properties	Single filament fineness	Denier	—	—	—	—	—	3.5
	Weight per unit area	g/m <sup>2</sup>	—	—	—	—	—	30
	BSM strength	kg/5cm width	—	—	—	—	—	17
	Texture	—	—	—	—	—	—	Poor
	Biodegradability	—	—	—	—	—	—	Good

## Comparative Examples 3 and 4

Filament nonwoven fabrics were produced in the same way as in Example 1, except that the MFR value of the polymer was changed as shown in Table 2. Manufacturing conditions and spinnability in these comparative examples are shown in Table 2.

## Comparative Examples 5 and 6

Filament nonwoven fabrics were produced in the same way as in Example 1, except that the spinning temperature was changed as shown in Table 2. Manufacturing conditions and spinnability in these comparative examples are shown in Table 2.

## Comparative Example 7

A filament nonwoven fabric formed of filaments was produced in the same way as in Example 4, except that an embossing temperature of 113 °C was used for bonding operation with heat and pressure. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric produced in this comparative example are shown in Table 2.

As is apparent from Table 2, interfilament fusions did occur in Comparative Example 1, because the drafting speed was lower than 1000 m/min. This resulted in poor filament spreading-open effect and, therefore, no sheeting of good texture could be obtained.

In Comparative Example 2, a drafting speed higher than 5,000 m/min. was used and this resulted in poor draft efficiency in a high-speed air current. As such, filament breaks frequently occurred and this prevented sheet formation.

In Comparative Example 3, the MFR value was higher than 100 g/10 min. and this resulted in poor draft efficiency in a high-speed air current. As such, filament breaks frequently occurred and this prevented sheet formation.

In Comparative Example 4, the MFR value was less than 10 g/10 min. and this resulted in poor draft efficiency in a high-speed air current, which in turn adversely affected spinnability.

In Comparative Example 5, the spinning temperature was lower than  $(T_m + 20)^\circ\text{C}$ , where  $T_m$  is the melting point of the polymer, and this resulted in poor draft efficiency in a high-speed air current, which in turn adversely affected spinnability.

In Comparative Example 6, the spinning temperature was higher than  $(T_m + 80)^\circ\text{C}$ , where  $T_m$  is the melting point of the polymer, and this slowed down the process of crystallization in the quenching stage and, in the meantime, thermal degradation of the polymer proceeded. As a result, interfilament adhesion did occur, which in turn resulted in poor filament spreading-open effect. Therefore, no sheeting of good texture could be obtained.

In Comparative Example 7, the embossing temperature was higher than the melting point of the polymer and, therefore, the nonwoven fabric obtained was unsatisfactory in respect of flexibility and texture.

## Example 9

An L-lactic acid-hydroxycaproic acid copolymer of L-lactic acid / hydroxycaproic acid = 90 / 10 mol % which has a melting point of 168 °C and an MFR value of 20 g/10 min. was melt spun into filaments through a circular spinneret at a spinning temperature of 195°C and at a mass out flow rate from each orifice of 1.75 g/min. Filaments spun were quenched by a conventional quenching device, and were then drafted and attenuated at a drafting speed of 4,500 m/min. Filaments were spread open and deposited on a collecting surface of a travelling conveyor, being thus formed into a web. The web was then passed through a partial bonding apparatus with heat and pressure comprising embossing rolls wherein partial bonding with heat and pressure was carried out under the following conditions: roll temperature of 108°C; linear roll pressure of 10 kg/cm; and pressure bonded area ratio of 7.6 %. Subsequently, the web obtained was placed on a wire cloth of 30 mesh travelling at a velocity of 30 m/min. and was subjected to treatment by pressurized liquid. The treatment by pressurized liquid was carried out by means of a pressurized columnar water jet treatment apparatus having jet holes, each of 0.12 mm in diameter, arranged at hole intervals of 1.0 mm and in three arrays, in such a way that the pressure of columnar water streams was applied over the web from the position 80 mm above the web, with the pressure set at 60 kg/cm<sup>2</sup> G. Also, similar treatment was applied to both sides of the web, once for each side. Then, the so treated product was subjected to removal of excess moisture therefrom by means of mangle rolls. Thereafter, the web was subjected to drying by a hot air drier at 60°C. As a result, a filament nonwoven fabric comprised of filaments having a single filament fineness of 3.5 denier was obtained, the nonwoven fabric having a weight per unit area of 30 g/m<sup>2</sup>. It was found that bonded areas with heat and pressure as previously formed in the filament nonwoven fabric had been completely released from bond by the pressurized water jet treatment. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 9 are shown in Table 3.

TABLE 3

		Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17
Polymer	MFR value	g/min	20	20	20	20	10	100	20	20
	p-lactic acid copolymerization ratio	mol%	0	0	20	0	0	0	0	0
	L-lactic acid copolymerization ratio	mol%	90	70	80	100	Note 1 100	90	90	90
	Hydroxyacetic acid copolymerization ratio	mol%	10	30	0	0	0	10	10	10
	Melting point	°C	168	139	112	178	178	168	168	168
Manufacturing conditions	Spinning temperature	°C	195	165	135	205	205	195	185	215
	Single-hole discharge rate	g/min	1.75	1.35	1.24	1.79	1.67	1.24	1.46	1.56
	Drafting speed	m/min	4500	3500	3200	4600	4300	3800	4000	3400
	Excess temperature	°C	108	79	52	118	118	108	108	108
	Linear pressure by rolling	kg/cm	10	10	10	10	10	10	10	10
Operational performance	Adhesion	—	None	None	None	None	None	None	None	None
	Filament break	—	None	None	None	None	None	None	None	None
	Filament Spreading-open efficiency	—	Good	Good	Good	Good	Good	Good	Good	Good
Nonwoven properties	Single filament fineness	Denier	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
	Weight per unit area	g/m <sup>2</sup>	30	30	30	30	30	30	30	30
	KSM strength	kg/5cm width	12	9	6	15	15	12	10	12
	Texture	—	Good	Good	Good	Good	Good	Good	Good	Good
Biodegradability	Biodegradability	—	Good	Good	Good	Good	Good	Good	Good	Good

Note 1: L-lactic acid polymer was added with 1 wt% talc as crystallizing agent.

Example 10

The copolymerization ratio of L-lactic acid and hydroxycaproic acid in the L-lactic acid-hydroxycaproic acid copoly-

mer; spinning temperature; mass out flow rate from each orifice; spinning velocity; and embossing temperature were changed as shown in Table 3. In other respects, the same procedure as used in Example 9 was followed to obtain a filament nonwoven fabric. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 10 are shown in Table 3.

#### Example 11

A copolymer of L-lactic acid / D-lactic acid = 80 / 20 mol % was used. The spinning temperature, mass out flow rate, spinning velocity, and embossing temperature were changed as shown in Table 3. In other respect, the same procedure as used in Example 9 was followed to obtain a filament nonwoven fabric. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 11 are shown in Table 3.

#### Example 12

Poly(L-lactic acid) was used. The spinning temperature, mass out flow rate, spinning velocity, and embossing temperature were changed as shown in Table 3. In other respect, operation was carried out in the same way as in Example 9 to obtain a filament nonwoven fabric. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 12 are shown in Table 3.

#### Example 13

A filament nonwoven fabric was produced in the same way as in Example 12, except that a composition comprising poly(L-lactic acid) and 1 wt % talc added thereto as a crystallizing agent was used, and except that the mass out flow rate from each orifice and spinning velocity were changed as shown in Table 3. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 13 are shown in Table 3.

#### Examples 14 and 15

A filament nonwoven fabric was produced in the same way as in Example 9, except that the MFR value of the polymer was changed as shown in Table 3, and except that the mass out flow rate from each orifice and the spinning velocity were changed as shown in Table 3. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in these Examples are shown in Table 3.

#### Examples 16 and 17

A filament nonwoven fabric was produced in the same way as in Example 9, except that the spinning temperature, mass out flow rate from each orifice, and spinning velocity were changed as shown in Table 3. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in these Examples 16 and 17 are shown in Table 3.

#### Examples 18 and 19

A filament nonwoven fabric was produced in the same way as in Example 9, except that the embossing temperature, and associated linear pressure of a roll set were changed as shown in Table 4. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in these Examples 18 and 19 are shown in Table 4.

TABLE 4

			Example 18	Example 19	Example 20	Comparative Example 8	Comparative Example 9
Polymer	MFR value	g/10min	20	20	20	20	20
	D-lactic acid copolymerization ratio	mol%	0	0	0	0	0
	L-lactic acid copolymerization ratio	mol%	90	90	90	90	90
	Hydroxyacrylic acid copolymerization ratio	mol%	10	10	10	10	10
Manufacturing conditions	Melting point	°C	168	168	168	168	168
	Spinning temperature	°C	195	195	195	195	195
	Single-hole discharge rate	g/min	1.75	1.75	1.75	1.75	1.75
	Drafting speed	m/min	4500	4500	4500	4500	4500
	Emboss temperature	°C	88	118	108	140	108
Operational performance	Linear pressure by rolling	kg/cm	30	5	10	5	50
	Adhesion	—	None	None	None	None	None
	Filament break	—	None	None	None	None	None
	Filament Spreading-open efficiency	—	Good	Good	Good	Good	Good
	Single filament fineness	Denier	3.5	3.5	3.5	3.5	3.5
Nonwoven fabric properties	Weight per unit area	g/m <sup>2</sup>	30	30	170	30	30
	RCSM strength	kg/5cm width	11	15	6	8	5
	Texture	—	Good	Good	Good	Poor	Poor
	Biodegradability	—	Good	Good	Good	Good	Good

Example 20

Six sheets of bonded webs with heat and pressure obtained in Example 9, placed one over another, were needle-punched for three-dimensionally-entangling treatment. In other respects, the same procedure as used in Example 9 was followed to produce a filament nonwoven fabric. Specifically, a laminated web structure consisting of 6 sheets of webs having partial temporary bonded areas with heat and pressure formed in the same way as in Example 9 was sub-

jected to needle punching by punching needles of #40 regular barb, under conditions setting of: needle depth, 11 mm; and punching density, 200 punches/cm<sup>2</sup>. As a result, a filament nonwoven fabric was obtained wherein individual filaments were three-dimensionally entangled and temporary bonded areas with heat and pressure were partially retained as such. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 20 are shown in Table 4.

#### Comparative Example 8

The embossing temperature and roll linear pressure of a roll set in embossing operation were respectively changed to 140°C and 5 kg/cm. In other respects, partial bonding with heat and pressure and subsequent three-dimensional entangling were carried out in the same way as in Example 9 to produce a filament nonwoven fabric. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Comparative Example 8 are shown in Table 4.

#### Comparative Example 9

The embossing temperature and roll linear pressure of a roll set in embossing operation were respectively changed to 108°C and 50 kg/cm. In other respects, operation was carried out in the same way as in Example 9 to produce a filament nonwoven fabric. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Comparative Example 9 are shown in Table 4.

As may be apparent from Tables 3 and 4, filament nonwoven fabrics obtained in Examples 9 to 20 were all three-dimensionally entangled nonwoven fabrics in which more than certain proportions of temporary bonded areas with heat and pressure had disappeared, and had sufficient strength to enable the fabric to serve for practical purposes. The nonwoven fabrics also had very good biodegradability such that when removed from a compost in which these nonwoven fabrics had been buried, all the fabrics were found as having undergone considerable decrease in weight, substantial changes in configuration, and considerable degradation in strength maintenance.

In Example 18 in particular, since a considerably low embossing temperature was used, the filament nonwoven fabric obtained was such that with temporary bonded areas with heat and pressure completely released from bond, the fabric had a three-dimensionally entangled configuration. Therefore, the nonwoven fabric had sufficient strength for serving practical purposes. Also, the fabric was found very satisfactory in biodegradation performance.

In Example 19, the use of a somewhat higher embossing temperature, coupled with the fact that a somewhat lower linear pressure of a roll set was used, led to the disappearance of about one third of the area of partial temporary bonded areas with heat and pressure; and in addition, individual filaments other than those at bonded areas with heat and pressure were found to have been three-dimensionally entangled. Because of the effect of the remaining temporary bonded areas with heat and pressure, and because of the effect of the three-dimensional entanglement, the nonwoven fabric exhibited some improvement in strength characteristics, and also good biodegradation performance.

Whilst, in Comparative Example 8, since the embossing temperature was too high, despite the fact that linear pressure of a roll set was set low, there was found little effect of entanglement by pressured-liquid-stream treatment with respect to constituent filaments. Fluffs were found on the fabric surface. The fabric was of poor appearance quality.

In Comparative Example 9, since the roll linear pressure of a roll set was too high, despite the fact that embossing temperature was set low, there was found little effect of entanglement by pressured-liquid-stream treatment with respect to constituent filaments. Fluffs were found on the fabric surface. The fabric was of poor appearance quality.

#### Example 21

An L-lactic acid-hydroxycaproic acid copolymer of L-lactic acid / hydroxycaproic acid = 90 / 10 mol % which had a melting point of 168 °C and an MFR value of 20 g/10 min. was melt spun into filaments through a circular spinneret at a spinning temperature of 195°C and at a mass out flow rate from each orifice of 1.75 g/min. Filaments spun were quenched by a conventional quenching device, using air current of 20°C, and were then drafted and attenuated at a drafting speed of 4,500 m/min. Filaments were spread open each other and deposited on a collecting surface of a travelling conveyor. Then, the filaments were subjected to partial temporary bonding with heat and pressure by an embossing roll heated to 108°C, whereby a web was formed. Six sheets of webs thus formed were placed one over another, and the superposed sheets of web were needle-punched, 200 punches / cm<sup>2</sup>, by #40 regular needles, whereby constituent filaments were three-dimensionally entangled. The three-dimensionally entangled web was subjected, at one side only, to overall bonding with heat and pressure by a Yankee drier (made by Kumagai Riki Kogyo K. K.) under the following operating conditions: surface temperature, 170°C; heat treat time, 100 seconds, and linear pressure of a roll set, 0.5 kg/cm. Thus, a filament nonwoven fabric having a weight per unit area of 170 g/m<sup>2</sup> was obtained. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Examples 21 are shown in Table 5(a).

TABLE 5(a)

Polymer	MFR value	Example 21				Example 22				Example 23				Example 24				Example 25			
		g/10min				20				20				20				20			
Polymer	D-lactic acid copolymerization ratio	mol%				0				0				0				0			
	L-lactic acid copolymerization ratio	mol%				90				70				80				100			
	Hydroxyacetic acid copolymerization ratio	mol%				10				30				0				0			
	Melting point	°C				108				139				112				178			
	Fiber cross section	—				Solid				Solid				Solid				Solid			
Manufacturing conditions	Spinning temperature	°C				105				105				105				205			
	Flow rate	g/min				1.75				1.35				1.24				1.79			
	Drafting speed	m/min				4500				3500				3200				4300			
	Operating temperature with heat and pressure	°C				170				141				114				180			
	Linear pressure	kg/cm				0.5				0.5				0.5				0.5			
Operational performance	Adhesion	—				None				None				None				None			
	Filament break	—				None				None				None				None			
	Filament spreading-open efficiency	—				Good				Good				Good				Good			
	Single filament fineness	Denier				3.5				3.5				3.5				3.5			
	Weight per unit area	g/m <sup>2</sup>				170				170				170				30			
Nonwoven fabric properties	KCS strength	kg/5cm width				6				5				5				8			
	Texture	—				Good				Good				Good				Good			
	Biodegradability	—				Good				Good				Good				Good			

Note 1: L-lactic acid polymer was added with 1 wt% talc as crystallizing agent.



TABLE 5(b)

Polymer	MFR value	Example 26		Example 27		Example 28		Example 29	
		g/min	20	20	20	20	20	20	20
Polymer	D-lactic acid copolymerization ratio	mol%	0	0	10	0	0	0	0
	L-lactic acid copolymerization ratio	mol%	90	80	90	90	90	90	90
	Hydroxyacetic acid copolymerization ratio	mol%	10	Note 2	0	10	10	10	10
	Melting point	°C	138	111	141	138	138	138	138
	Fiber cross section	—	Solid	Divided type composite (Fig. 5)		Solid	Solid	Solid	Solid
Manufacturing conditions	Spinning temperature	°C	135	170	170	135	135	135	135
	Flow rate	g/min	3.00	1.59	1.75	1.75	1.75	1.75	1.75
	Drafting speed	m/min	5000	4100	4500	4500	4500	4500	4500
	Overall bonding with heat and pressure	Operating temperature	°C	170	115	Note 3	Note 3	Note 3	170
		Linear pressure	kg/cm	0.5	1.0	0.5	0.5	0.5	0.5
Operational performance	Adhesion	—	None	None	None	None	None	None	None
	Filament break	—	None	None	None	None	None	None	None
	Filament Spreading-open efficiency	—	Good	Good	Good	Good	Good	Good	Good
	Single filament fineness	Denier	5.4	3.5	3.5	3.5	3.5	3.5	3.5
	Weight per unit area	g/m <sup>2</sup>	170	280	150	150	150	150	150
Nonwoven fabric properties	KCSN strength	kg/5cm width	6	5	10	10	10	10	10
	Texture	—	Good	Good	Good	Good	Good	Good	Good
	Biodegradability	—	Good	Good	Good	Good	Good	Good	Good

Note 2: Glycolic acid was used in place of hydroxyacetic acid. Note 3: Bonding with heat and pressure was applied to both surfaces of web.

## Example 22

The copolymerization ratio of L-lactic acid to hydroxyacetic acid in the L-lactic acid-hydroxyacetic acid copolymer, and the spinning temperature, the mass out flow rate from each orifice, the drafting speed, and the Yankee drier

temperature were changed as shown in Table 5(a). The embossing roll temperature was set at 79°C. In other respects, operation was carried out in the same way as in Example 21 to obtain a filament nonwoven fabric. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained in this Example 22 are shown in Table 5(a).

#### Example 23

An L-lactic acid / D-lactic acid copolymer having a copolymerization ratio of L-lactic acid / D-lactic acid = 80 / 20 mol % was used. The spinning temperature, mass out flow rate from each orifice, drafting speed, and Yankee drier temperature were changed as shown in Table 5. The embossing roll temperature was set at 52°C. In other respects, operation was carried out in the same way as in Example 21 to obtain a filament nonwoven fabric. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained in this Example 23 are shown in Table 5(a).

#### Example 24

Poly(L-lactic acid) was used. The spinning temperature, mass out flow rate from each orifice, spinning velocity, and Yankee drier temperature were changed as shown in Table 5(a). The embossing roll temperature was set at 118°C. In other respects, operation was carried out in the same way as in Example 21 to obtain a filament nonwoven fabric. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained in this Example 24 are shown in Table 5(a).

#### Example 25

A composition comprising poly(L-lactic acid) and 1 wt% of talc added thereto as a crystallizing agent was used. The spinning temperature, mass out flow rate from each orifice, and spinning velocity were changed as shown in Table 5(a). In other respects, operation was carried out in the same way as in Example 24. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained in this Example 25 are shown in Table 5(a).

#### Example 26

A filament nonwoven fabric formed from filaments having a single filament fineness of 5.4 denier was produced in the same way as in Example 21, except that a mass out flow rate from each orifice of 3.00 g / min. and a drafting speed of 5,000 m/min were used. The manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric obtained in this Example 26 are shown in Table 5(b).

#### Example 27

A copolymer of L-lactic acid / glycolic acid = 80 / 20 mol% having a melting point of 111°C. and an MFR value of 20 g / 10 min. was used as a first component, and a poly(D, L-lactic acid) of L-lactic acid/D-lactic acid = 90 / 10 mol% having a melting point of 141°C and an MFR value of 20 g/10 min. was used as a second component, the two components being used in the ratio of 1 / 1 by weight. The two components were melt spun through a spinneret having a nozzle configuration such that in a split type composite section as shown in Fig. 5, the first component was disposed at the core side and the second component at the leaf side, with a spinning temperature set at 170°C and a mass out flow rate from each orifice of 1.59 g/min. Filaments spun were quenched by a conventional quenching device, and were then drafted and attenuated at a drafting speed of 4,100 m/min., then spread open each other and deposited on a collecting surface of a travelling conveyor, being then passed through rollers at an emboss temperature of 51°C and a roll linear pressure of a roll set of 10 kg/cm, whereby a nonwoven web of 300 g/m<sup>2</sup> was formed. Then, the web was needle-punched, 200 punches / cm<sup>2</sup>, by #40 regular needles, whereby constituent filaments were three-dimensionally entangled. The three-dimensionally entangled web was subjected, at one side only, to overall bonding with heat and pressure by a Yankee drier (made by Kumagai Riki Kogyo K. K.) under the following operating conditions: surface temperature, 115°C; heat treat time, 100 seconds, and linear pressure of a roll set, 1.0 kg/cm. Thus, a biodegradable composite filament nonwoven fabric having a weight per unit area of 280 g/m<sup>2</sup> was obtained. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Examples 27 are shown in Table 5(b).

#### Example 28

A filament nonwoven sheet which had undergone an overall bonding with heat and pressure on one side only was obtained in the same way as in Example 21. This sheet, turned over, was again subjected to overall bonding with heat

and pressure under the same conditions. Thus, a both-side bonded type nonwoven fabric having a weight per unit area of 150 g/m<sup>2</sup> was obtained. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 28 are shown in Table 5(b).

#### 5 Example 29

A filament nonwoven fabric similar to Example 21 except the weight per unit area which was changed to 100 g/m<sup>2</sup> was produced. This filament nonwoven fabric was subjected to overall bonding with heat and pressure on one side only under the same conditions as in Example 21. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Example 29 are shown in Table 5(b).

As is apparent from Table 5(a) and Table 5(b), each nonwoven fabrics obtained in Examples 21 to 29 have excellent tensile strength of 5 kg/5 cm width or more. Further, these nonwoven fabrics have good air tightness and water proof, and when taken out after having been buried in a compost, each nonwoven fabrics were found to have been largely decreased in weight, changed in configuration to a great extent and remarkably decreased in strength retained.

#### 15 Comparative Example 10

A filament nonwoven fabric was obtained in the same way as in Example 21, except that the operating temperature for overall bonding with heat and pressure was set at 180°C. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Comparative Example 10 are shown in Table 6.

TABLE 6

25				Comparative Example 10	Comparative Example 11	Comparative Example 12
	Polymer	MFR value	g/10 min	20	20	20
30		D-lactic acid copolymerization ratio	mol%	0	0	0
		L-lactic acid copolymerization ratio	mol%	90	90	90
		Hydroxycaproic acid copolymerization ratio	mol%	10	10	10
		Melting point	°C	168	168	168
40	Manufacturing conditions	Fiber cross section	-	Solid	Solid	-
		Spinning temperature	°C	195	195	-
		Flow rate	g/min	1.75	1.75	-
		Drafting speed	m/min	4500	4500	-
		Overall bonding with heat and pressure	Operating temperature	°C	180	170
45			Linear pressure	kg/cm	0.5	15
50	Operational performance	Adhesion	-	None	None	-
		Filament break	-	None	None	-
		Filament Spreading-open efficiency	-	Good	Good	-
55	Nonwoven fabric properties	Single filament fineness	Denier	3.5	3.5	-
		Weight per unit area	g/m <sup>2</sup>	-	170	170
		KGSM strength	kg/5cm width	-	9	72
		Texture	-	-	Good	Good
		Biodegradability	-	-	Good	Good

## Comparative Example 11

A filament nonwoven fabric was obtained in the same way as in Example 21, except that the linear pressure of a roll set for overall bonding with heat and pressure was changed as shown in table 6. Manufacturing conditions, spinnability, and properties and biodegradability of the nonwoven fabric in this Comparative Example 11 are shown in Table 6.

## Comparative Example 12

A sheet-form film of the same 170 g/m<sup>2</sup> weight per unit area as that in Example 21 was produced by using an L-lactic acid-hydroxycaproic acid copolymer of L-lactic acid / hydroxycaproic acid = 90 / 10 mol % which had a melting point of 168 °C and an MFR value of 20 g/10 min. The properties of this film is shown in Table 6.

As may be apparent from Table 6, in Comparative Example 10, a temperature which was 12°C higher than the melting temperature of the copolymer was used as the operating temperature for overall bonding with heat and pressure. This caused sheet adhesion to the process machine, which did not allow production of a nonwoven fabric.

In Comparative Example 11, linear pressure of a roll set applied to bonding with heat and pressure was too high that the produced nonwoven fabric was in a form of a film lacking flexibility.

In Comparative Example 12, the product was of a complete film form and had no nonwoven structure in its interior. Therefore, the product lacked flexibility and could not serve for practical use.

## Example 30

A polybutylene succinate (number-average molecular weight: 50,000) having a melting point of 116°C and an MFR value of 30 g/10 min., and containing 1 wt % of talc, was used. This polymer was melt spun through a circular spinneret at a spinning temperature of 190°C and at a mass out flow rate from each orifice of 0.67 g/min. Filaments spun were quenched by a conventional quenching device, and were then drafted and attenuated at a drafting speed of 2,000 m/min. Filaments were spread open each other and deposited on a collecting surface of a travelling conveyor, being thus formed into a web. The web was then passed through a partial bonding apparatus with heat and pressure comprising embossing rolls wherein partial bonding with heat and pressure was carried out under the following conditions: roll temperature of 90°C; and pressure bonded area ratio of 7.6 %. Thus, a filament nonwoven fabric comprised of filaments having a single filament fineness of 3.0 denier, with a weight per unit area of 60 g/m<sup>2</sup>, was obtained. The constituent filaments of the web had a crystallization degree of 18 % and a supercool index of 0.41.

The filament nonwoven fabric obtained was preheated to 80°C and by using a mold the preheated nonwoven fabric was formed into a conical coffee filter having an opening diameter of 8.5 cm and a depth of 4.5 cm. This coffee filter was a good formed piece. The formed piece had an air permeability of 120 cc/cm<sup>2</sup> /sec. The formed filter was put into a continuous composting arrangement, and in about one month it had been composted leaving no trace of it.

## Example 31

An L-lactic acid / hydroxycaproic acid copolymer (number-average molecular weight: 90,000; weight ratio = 88/12) having a melting point of 162°C and an MFR value of 20 g/10 min., and containing 1 wt % of boron nitride, was used. This polymer was melt spun through a spinneret identical to the one used in Example 29 at a spinning temperature of 200°C and at a mass out flow rate from each orifice of 0.89 g/min. Filaments spun were quenched by a conventional quenching device, and were then drafted and attenuated at a drafting speed of 2,000 m/min. Filaments were spread open each other and deposited on a travelling conveyor, being thus formed into a web. The web was then passed through a partial bonding apparatus with heat and pressure comprising embossing rolls wherein partial bonding with heat and pressure was carried out under the conditions of roll temperature, 132°C, and pressure bonded area ratio, 6.5 %. Thus, a filament nonwoven fabric comprised of filaments having a single filament fineness of 4.0 denier, with a weight per unit area of 65 g/m<sup>2</sup>, was obtained. The constituent filaments of the web had a crystallization degree of 21 % and a supercool index of 0.52.

The filament nonwoven fabric obtained was preheated to 120°C and was formed by pressing into a plant pot having an opening diameter of 10.5 cm and a depth of 5.5 cm. In this way, good formed piece was obtained. The formed plant pot had an air permeability of 170 cc/cm<sup>2</sup> /sec. A plant potted in this formed plant pot was set, together with the pot, for growth in the ground at an intended location. The plant smoothly grew into a mature tree. Three years after the plant in the plant pot was initially set in the ground, it was found that the plant pot had been degraded in the earth with no trace left of it.

## Examples 32 and 33

A copolymer of L-lactic acid / glycolic acid = 80 / 20 mol% having a melting point of 111°C, an MFR value of 30 g / 10 min. and a number average molecular weight of 70,000 was used as a low melting point component in Fig. 5, and a poly(D, L-lactic acid) of L-lactic acid/D-lactic acid = 90 / 10 mol% having a melting point of 141°C, an MFR value of 20 g/10 min. and a number average molecular weight of 90,000 was used as a high melting point component, the two components being used in the ratio of high melting point component / low melting point component = 1 / 1 by weight. The two components were melt spun through a spinneret having a nozzle configuration such that in a split type composite cross section as shown in Fig. 5, the low melting point component was disposed at the core side and the high melting point component at the leaf side, with a spinning temperature set at 170°C and a mass out flow rate from each orifice of 1.36 g/min. Filaments spun were quenched by a conventional quenching device, and were then drafted and attenuated at a drafting speed of 1,500 m/min., then spread open each other and deposited on a collecting surface of a travelling conveyor. Then, the filaments were subjected to temporary bonding with heat and pressure under the conditions of: embossing temperature, 51°C; linear pressure of a roll set, 10 kg/cm; pressure bonded area ratio, 6.5 %; and pressure bonded spot density, 36 bonded areas per cm<sup>2</sup>, whereby a nonwoven web was formed. Then, the web was subjected to a three-dimensionally-entangling treatment by pressured liquid streams. That is, the nonwoven web was placed on a moving wire net (of 48 mesh) and exposed to jet streams of pressure liquid. For this purpose, an apparatus having orifices arranged in three rows, each orifice having a hole diameter of 0.2 mm and inter-hole spacing of 0.4 mm, was employed. For the pressure liquid, water was used. Two kinds of jet pressure were used, namely, 40 kg / cm<sup>2</sup> G x 4 times (Example 32), and 100 kg / cm<sup>2</sup> G x 4 times (Example 33). Excess water in the web was removed by means of mangle rolls, and then the web was dried. In Example 32, in which the jet pressure applied was 40kg/cm<sup>2</sup>G, the nonwoven fabric obtained was a three-dimensionally entangled nonwoven fabric, with temporary bonded areas with heat and pressure left unremoved. In Example 33, in which the jet pressure applied was 100 kg / cm<sup>2</sup> G, the nonwoven fabric obtained had constituent filaments thereof three-dimensionally entangled all over, with temporary bonded areas with heat and pressure completely separated. These nonwoven fabrics had a weight per unit area of 70 g/m<sup>2</sup>. Their constituents filaments had a single-filament fineness of 3.5 denier, a crystallization degree of 16 %, and a supercool index of 0.6.

The filament nonwoven fabrics thus obtained were each preheated to 100°C and formed by pressing into a plant pot having an opening diameter of 10.5 cm and a depth of 5.5 cm. In this way, good formed pieces were obtained. The formed plant pots, of both Examples 32 and 33, had an air permeability of about 160 cc/cm<sup>2</sup> sec. A plant potted in each formed plant pot was set, together with the pot, for growth in the ground at an intended location. The plant smoothly grew into a mature tree. Three years after the plant in the plant pot was initially set in the ground, it was found that the plant pot had been degraded in the earth with no trace left of it.

### 35 Claims

1. A nonwoven fabric made up of filaments comprised of a polylactic acid-based polymer, wherein the polylactic acid-based polymer is a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, said polymer having a melting point of 100°C or more, or a blend of such polymers having a melting point of 100°C or more.
2. A nonwoven fabric as set forth in claim 1, wherein constituent filaments of the nonwoven fabric are partially bonded with heat and pressure.
3. A nonwoven fabric as set forth in claim 1, wherein the nonwoven fabric has a spottedly fusion bonded portion such that individual filaments at partially preformed temporary bonded areas with heat and pressure are partially separated from one another by a three-dimensionally-entangling treatment, and wherein individual filaments at other area than the spottedly fusion bonded area which is not fusion-bonded are three-dimensionally entangled together so as to be integrated as a whole.
4. A nonwoven fabric as set forth in claim 1, wherein individual filaments at partially preformed temporary bonded areas with heat and pressure are completely separated from one another by a three-dimensionally entangling treatment whereby they are three-dimensionally entangled with one another so as to be integrated as a whole.
5. A nonwoven fabric as set forth in claim 2, wherein at least one side of a web comprised of filaments is bonded with heat and pressure all over.
6. A nonwoven fabric as set forth in claim 3, wherein at least one side of a web comprised of filaments is bonded with

heat and pressure all over.

7. A nonwoven fabric as set forth in claim 1, wherein the cross section of each constituent filament is either a solid or open hollow cross section or a polygonal or planar odd-shaped cross section.
8. A nonwoven fabric made up of filaments comprised of a polylactic acid-based polymer as set forth in claim 1, wherein the cross section of each constituent filament is a sheath-core type composite cross section of a bi-component filament.
9. A nonwoven fabric made up of filaments comprised of a polylactic acid-based polymer as set forth in claim 1, wherein the cross section of each constituent filament is a split type composite cross section such that bi-components of the filament have their respective geometric forms separate from each other which both continuously extend as such in the direction of filament axis and are exposed on the surface of the filament.
10. A nonwoven fabric as set forth in claim 1, wherein the filaments have a single filament fineness of from 1 to 12 deniers.
11. A nonwoven fabric as set forth in claim 1, wherein the nonwoven fabric has a weight per unit area of from 10 to 500 g/m<sup>2</sup>.
12. A nonwoven fabric as set forth in claim 1, wherein the nonwoven fabric has a tensile strength of not less than 5 kg/5 cm width as measured on the basis of a weight per unit area of 100 g/m<sup>2</sup>.
13. A method of fabricating a nonwoven fabric made up of filaments comprised of a polylactic acid-based polymer, comprising the steps of melting a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, said polymer having a melting point of 100°C or more, or a blend of such polymers having a melting point of 100°C or more, said polymer or polymer blend having a melt flow rate of from 10 to 100 g/10 minutes as measured at 190°C according to ASTM-D-1238 (E), in a temperature range of from (T<sub>m</sub> + 20)°C to (T<sub>m</sub> + 80)°C, where T<sub>m</sub>°C is the melting point of the polymer or polymer blend; extruding the melt through a spinneret into filaments; drafting the extruded filaments by means of a suction device at a drafting speed of from 1,000 to 5,000 m/minute, thereby fining them down into finer filaments; depositing such filaments, as they are spread open each other, and are laid up on a travelling collector surface to form a web; and heat-treating the web thereby to obtain the nonwoven fabric.
14. A fabricating method as set forth in claim 13, wherein constituent filaments of the web are partially bonded with heat and pressure bonded at a temperature lower than the melting point of the polymer or polymer blend.
15. A fabricating method as set forth in claim 14, wherein two or more kinds of components comprising said polymer or polymer blend are melt spun into filaments by means of a spinneret which provides a composite sectional configuration with respect to the fiber cross section of each of the filaments, and wherein said partial bonding with heat and pressure is effected at a temperature lower than the melting point of one of said two or more kinds of components which is lowermost of their melting points.
16. A fabricating method as set forth in claim 13, which further comprises subjecting the web to partial bonding with heat and pressure thereby to form temporary bonded areas with heat and pressure, then effecting a three-dimensionally entangling treatment with respect to the web thereby to cause individual filaments at the temporary bonded areas with heat and pressure to be at least partially separated, and three-dimensionally-entangling individual filaments in the separated condition thereby to integrate filaments of the web as a whole.
17. A fabricating method as set forth in claim 16, wherein the step of partial bonding with heat and pressure for forming temporary bonded areas with heat and pressure is carried out by pressing the web by an embossing roll, said partial bonding with heat and pressure being effected at a processing temperature of from (T<sub>m</sub> - 80) °C to (T<sub>m</sub> - 50) °C, where T<sub>m</sub>°C is the melting point of one of the constituent components of individual filaments which is lowermost of the melting points of the components, with linear pressure of a roll set within a range of from 5 to 30 kg/cm.
18. A fabricating method as set forth in claim 13, wherein the web, formed by depositing filaments on the travelling collector surface as they are spread open, is subjected to partial temporary bonding with heat and pressure, at least one side of the web being subsequently bonded with heat and pressure all over.

19. A fabricating method as set forth in claim 18, wherein the step of bonding with heat and pressure all over is carried out at a temperature of not more than  $(T_m + 10)^{\circ}\text{C}$  and under linear pressure of a roll set of 0.01 kg/cm or more.
20. A fabricating method as set forth in claim 18, wherein two or more kinds of components comprising said polymer or polymer blend are melt spun into filaments by means of a spinneret which provides a composite sectional configuration with respect to the filament cross section of each of the filaments, and wherein said all-over bonding with heat and pressure is effected at a temperature of not more than  $(T_m + 5)^{\circ}\text{C}$ , where  $T_m^{\circ}\text{C}$  is the highest melting point of the two or more kinds of components.
21. A fabricating method as set forth in claim 13, wherein the web, formed by depositing filaments on the travelling collector surface as they are spread open, is first subjected to partial temporary bonding with heat and pressure and then to three-dimensional entangling, at least one side of the web being subsequently bonded with heat and pressure all over.
22. A fabricating method as set forth in claim 21, wherein two or more kinds of components comprising said polymer or polymer blend are melt spun into filaments by means of a spinneret which provides a composite sectional configuration with respect to the cross section of each of the filaments, and wherein said all-over bonding with heat and pressure is effected at a temperature of not more than  $(T_m + 5)^{\circ}\text{C}$ , where  $T_m^{\circ}\text{C}$  is the highest melting point of said two or more kinds of components.
23. A nonwoven fabric made up of filaments comprised of a biodegradable polymer composed principally of a thermoplastic aliphatic polyester, wherein the filaments have a crystallization degree of 7 to 40% and a supercool index of 0.4 or more.
24. A nonwoven fabric as set forth in claim 23, wherein the biodegradable polymer comprises a polylactic acid-based polymer, said polylactic acid-based polymer being a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, or a blend of such polymers.
25. A nonwoven fabric as set forth in claim 23, wherein the biodegradable polymer is a polymer selected from the group consisting of polybutylene succinate, polyethylene succinate, polybutylene adipate, and polybutylene sebacate, or a copolymer in which such polymers are present as main repeating units.
26. A nonwoven fabric as set forth in claim 23, wherein the biodegradable polymer is added with a crystallizing agent.
27. A nonwoven fabric as set forth in claim 23, wherein constituent filaments are partially bonded with heat and pressure.
28. A nonwoven fabric as set forth in claim 23, wherein the nonwoven fabric has spottedly fusion bonded areas such that individual filaments at partially preformed temporary bonded areas with heat and pressure are partially separated from one another by a three-dimensionally entangling treatment, and wherein individual filaments at other areas than the spottedly fusion bonded areas which are not fusion-bonded are three-dimensionally entangled together so as to be integrated as a whole.
29. A nonwoven fabric as set forth in claim 23, wherein individual filaments at partially preformed temporary bonded areas with heat and pressure are completely separated from one another by a three-dimensionally entangling treatment whereby they are three-dimensionally interlaced with one another so as to be integrated as a whole.
30. A nonwoven fabric as set forth in claim 23, wherein the nonwoven fabric is thermoformable.
31. A nonwoven fabric as set forth in claim 30, wherein the biodegradable polymer comprises a polylactic acid-based polymer, said polylactic acid-based polymer being a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, or a blend of such polymers, said polylactic acid-based polymer having a number-average molecular weight of from 50,000 to 95,000.
32. A method of fabricating a nonwoven fabric made up of filaments comprised of a biodegradable polymer composed principally of a thermoplastic aliphatic polyester, comprising the steps of melting the biodegradable polymer, said biodegradable polymer having a melt flow rate of 10 to 100 g/10 minutes as measured at  $190^{\circ}\text{C}$  according to

ASTM-D-1238 (E), in a temperature range of from  $(T_m + 20)^\circ\text{C}$  to  $(T_m + 80)^\circ\text{C}$ , where  $T_m^\circ\text{C}$  is the melting point of the biodegradable polymer; extruding the melt through a spinneret into filaments; drafting the extruded filaments by means of a suction device disposed below the spinneret under a quenching air blow of not more than  $20^\circ\text{C}$  generated through a conventional device and at a drafting speed of from 1,000 to 5,000 m/minute, thereby fining them down into finer filaments; then depositing such filaments, as they are spread open each other, and are laid up on a travelling collector surface to form a web; and heat treating the web thereby to obtain the nonwoven fabric.

33. A fabricating method as set forth in claim 32, wherein the biodegradable polymer is a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, or a blend of such polymers.
34. A fabricating method as set forth in claim 32, wherein the biodegradable polymer is a polymer selected from the group consisting of polybutylene succinate, polyethylene succinate, polybutylene adipate, and polybutylene sebacate, or a copolymer in which such polymers are present as main repeating units.
35. A fabricating method as set forth in claim 32, wherein a crystallizing agent is added to the biodegradable polymer.
36. A fabricating method as set forth in claim 32, wherein constituent filaments of the web are partially bonded with heat and pressure at a temperature lower than the melting point of the biodegradable polymer.
37. A fabricating method as set forth in claim 36, wherein two or more kinds of components comprising said biodegradable polymer are melt spun into filaments by means of a spinneret which provides a composite sectional configuration with respect to the cross section of each of the filaments, and wherein said partial bonding with heat and pressure is effected at a temperature lower than the melting point of one of said two or more kinds of components which is lowermost of their melting points.
38. A fabricating method as set forth in claim 32, which further comprises subjecting the web to partial bonding with heat and pressure thereby to form temporary bonded areas with heat and pressure, then effecting a three-dimensionally entangling treatment with respect to the web thereby to cause individual filaments at the temporary bonded areas with heat and pressure to be at least partially separated, and three-dimensionally entangled individual filaments in the separated condition thereby to integrate filaments of the web as a whole.
39. A fabricating method as set forth in claim 38, wherein the step of partially bonding with heat and pressure for forming temporary bonded areas with heat and pressure is carried out by pressing the web by an embossing roll, said partial bonding with heat and pressure being effected at a processing temperature of from  $(T_m - 80)^\circ\text{C}$  to  $(T_m - 50)^\circ\text{C}$ , where  $T_m^\circ\text{C}$  is the melting point of one of the components of constituent filaments which is lowermost of the melting points of the components, with the linear pressure of the roll set within a range of from 10 to 100 kg/cm.
40. A fabricating method as set forth in claim 32, wherein the nonwoven fabric obtained is subjected to a thermoforming process.
41. A fabricating method as set forth in claim 40, wherein the biodegradable polymer comprises a polylactic acid-based polymer, said polylactic acid-based polymer being a polymer selected from the group consisting of poly(D-lactic acid), poly(L-lactic acid), copolymers of D-lactic acid and L-lactic acid, copolymers of D-lactic acid and hydroxy-carboxylic acid, and copolymers of L-lactic acid and hydroxy-carboxylic acid, or a blend of such polymers, said polylactic acid-based polymer having a number-average molecular weight of from 50,000 to 95,000.
42. A fabricating method as set forth in claim 32, wherein the drafting speed by the suction device during the process of drafting is 1,200 to 3,000 m/minute.



FIG.1

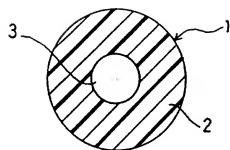


FIG.2



FIG.3

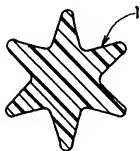


FIG.4

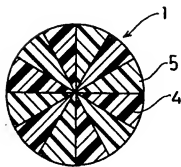


FIG.5

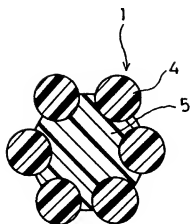
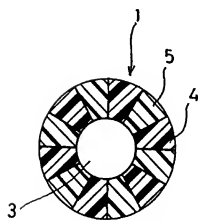


FIG.6





European Patent  
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## EUROPEAN SEARCH REPORT

Application Number  
EP 96 11 4791

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.4)
X	EP-A-0 597 427 (MITSUI TOATSU CHEMICALS) 18 May 1994	1,2,13	D04H1/42 D04H1/54 D04H1/48
A	* whole document *	3-6,14	
A	EP-A-0 671 496 (INT PAPER CO) 13 September 1995 * page 2, line 51 - line 54 *	3,4	
A	--- DATABASE WPI Section Ch, Week 9435 Derwent Publications Ltd., London, GB; Class A23, AN 94-283801 XP002023666 & JP-A-06 212 511 (UNITIKA LTD) , 2 August 1994 * abstract *	1,23,25	
A	EP-A-0 530 987 (MITSUI TOATSU CHEMICALS) 10 March 1993 * column 2, line 444 - column 25 *	1	
D,A	EP-A-0 637 641 (FIBERWEB SODOCA SARL) 8 February 1995 * page 2, line 48 - page 4, line 32 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.4)  D04H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 January 1997	Examiner V Beurden-Hopkins, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : number of the same patent family, corresponding document	

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